TEMPERATURE CONVERSION TABLES

—459.4 TO 0

C	F
—273	—459.4
—268	—450
—262	—440
—257	—430
—251	—420
—246	—410
—240	—400
—234	—390
—229	—380
—223	—370
—218	—360
—212	—350
—207	—340
—201	—330
—196	—320
—190	—310
—184	—300
—179	—290
—173	—280
—169	—273 — —459.4
—168	—270 — —454
—162	—260 — —436
—157	—250 — —418
—151	—240 — —400
—146	—230 — —382
—140	—220 — —364
—134	—210 — —346
—129	—200 — —328
—123	—190 — —310
—118	—180 — —292
—112	—170 — —274
—107	—160 — —256
—101	—150 — —238
— 96	—140 — —220
— 90	—130 — —202
— 84	—120 — —184
— 79	—110 — —166
— 73	—100 — —148
— 68	— 90 — —130
— 62	— 80 — —112
— 57	— 70 — — 94
— 51	— 60 — — 76
— 46	— 50 — — 58
— 40	— 40 — — 40
— 34	— 30 — — 22
— 29	— 20 — — 4
— 23	— 10 — 14
— 17.7	0 — 32

0 TO 100

C		F	C		F
—17.7	0	32	9.9	50	122.0
—17.2	1	33.8	10.4	51	123.8
—16.6	2	35.6	11.1	52	125.6
—16.1	3	37.4	11.5	53	127.4
—15.5	4	39.2	12.1	54	129.2
—15.0	5	41.0	12.6	55	131.0
—14.4	6	42.8	13.2	56	132.8
—13.9	7	44.6	13.7	57	134.6
—13.3	8	46.4	14.3	58	136.4
—12.7	9	48.2	14.8	59	138.2
—12.2	10	50.0	15.6	60	140.0
—11.6	11	51.8	16.1	61	141.8
—11.1	12	53.6	16.6	62	143.6
—10.5	13	55.4	17.1	63	145.4
—10.0	14	57.2	17.7	64	147.2
— 9.4	15	59.0	18.2	65	149.0
— 8.8	16	60.8	18.8	66	150.8
— 8.3	17	62.6	19.3	67	152.6
— 7.7	18	64.4	19.9	68	154.4
— 7.2	19	66.2	20.4	69	156.2
— 6.6	20	68.0	21.0	70	158.0
— 6.1	21	69.8	21.5	71	159.8
— 5.5	22	71.6	22.2	72	161.6
— 5.0	23	73.4	22.7	73	163.4
— 4.4	24	75.2	23.3	74	165.2
— 3.9	25	77.0	23.8	75	167.0
— 3.3	26	78.8	24.4	76	168.8
— 2.8	27	80.6	25.0	77	170.6
— 2.2	28	82.4	25.5	78	172.4
— 1.6	29	84.2	26.2	79	174.2
— 1.1	30	86.0	26.8	80	176.0
— .6	31	87.8	27.3	81	177.8
0	32	89.6	27.7	82	179.6
.5	33	91.4	28.2	83	181.4
1.1	34	93.2	28.8	84	183.2
1.6	35	95.0	29.3	85	185.0
2.2	36	96.8	29.9	86	186.8
2.7	37	98.6	30.4	87	188.6
3.3	38	100.4	31.0	88	190.4
3.8	39	102.2	31.5	89	192.2
4.4	40	104.0	32.1	90	194.0
4.9	41	105.8	32.6	91	195.8
5.5	42	107.6	33.3	92	197.6
6.0	43	109.4	33.8	93	199.4
6.6	44	111.2	34.4	94	201.2
7.1	45	113.0	34.9	95	203.0
7.7	46	114.8	35.5	96	204.8
8.2	47	116.6	36.1	97	206.6
8.8	48	118.4	36.6	98	208.4
9.3	49	120.2	37.1	99	210.2
			37.7	100	212.0

100 TO 1000

C		F	C		F
38	100	212	260	500	932
43	110	230	265	510	950
49	120	248	271	520	968
54	130	266	276	530	986
60	140	284	282	540	1004
65	150	302	288	550	1022
71	160	320	293	560	1040
76	170	338	299	570	1058
83	180	356	304	580	1076
88	190	374	310	590	1094
93	200	392	315	600	1112
99	210	410	321	610	1130
100	212	413	326	620	1148
104	220	428	332	630	1166
110	230	446	338	640	1184
115	240	464	343	650	1202
121	250	482	349	660	1220
127	260	500	354	670	1238
132	270	518	360	680	1256
138	280	536	365	690	1274
143	290	554	371	700	1292
149	300	572	376	710	1310
154	310	590	382	720	1328
160	320	608	387	730	1346
165	330	626	393	740	1364
171	340	644	399	750	1382
177	350	662	404	760	1400
182	360	680	410	770	1418
188	370	698	415	780	1436
193	380	716	421	790	1454
199	390	734	426	800	1472
204	400	752	432	810	1490
210	410	770	438	820	1508
215	420	788	443	830	1526
221	430	806	449	840	1544
226	440	824	454	850	1562
232	450	842	460	860	1580
238	460	860	465	870	1598
243	470	878	471	880	1616
249	480	896	476	890	1634
254	490	914	482	900	1652
			487	910	1670
			493	920	1688
			498	930	1706
			504	940	1724
			510	950	1742
			515	960	1760
			520	970	1778
			526	980	1796
			532	990	1814
			538	1000	1832

1000 TO 2000

C		F	C		F
538	1000	1832	815	1500	2732
543	1010	1850	820	1510	2750
549	1020	1868	827	1520	2768
554	1030	1886	831	1530	2786
560	1040	1904	838	1540	2804
565	1050	1922	842	1550	2822
571	1060	1940	849	1560	2840
576	1070	1958	853	1570	2858
582	1080	1976	860	1580	2876
587	1090	1994	864	1590	2894
593	1100	2012	871	1600	2912
598	1110	2030	876	1610	2930
604	1120	2048	882	1620	2948
609	1130	2066	887	1630	2966
615	1140	2084	893	1640	2984
620	1150	2102	898	1650	3002
626	1160	2120	904	1660	3020
631	1170	2138	909	1670	3038
637	1180	2156	915	1680	3056
642	1190	2174	920	1690	3074
648	1200	2192	926	1700	3092
653	1210	2210	931	1710	3110
659	1220	2228	937	1720	3128
664	1230	2246	942	1730	3146
670	1240	2264	948	1740	3164
675	1250	2282	953	1750	3182
681	1260	2300	959	1760	3200
686	1270	2318	964	1770	3218
692	1280	2336	970	1780	3236
697	1290	2354	975	1790	3254
704	1300	2372	981	1800	3272
708	1310	2390	986	1810	3290
715	1320	2408	992	1820	3308
719	1330	2426	997	1830	3326
726	1340	2444	1003	1840	3344
734	1350	2462	1008	1850	3362
737	1360	2480	1014	1860	3380
741	1370	2498	1019	1870	3398
748	1380	2516	1025	1880	3416
752	1390	2534	1030	1890	3434
760	1400	2552	1036	1900	3452
765	1410	2570	1041	1910	3470
771	1420	2588	1047	1920	3488
776	1430	2606	1052	1930	3506
782	1440	2624	1058	1940	3524
787	1450	2642	1063	1950	3542
793	1460	2660	1069	1960	3560
798	1470	2678	1074	1970	3578
804	1480	2696	1080	1980	3596
809	1490	2714	1085	1990	3614
			1093	2000	3632

2000 TO 3000

C		F	C		F
1093	2000	3632	1371	2500	4532
1098	2010	3650	1376	2510	4550
1104	2020	3668	1382	2520	4568
1109	2030	3686	1387	2530	4586
1115	2040	3704	1393	2540	4604
1120	2050	3722	1398	2550	4622
1126	2060	3740	1404	2560	4640
1131	2070	3758	1409	2570	4658
1137	2080	3776	1415	2580	4676
1142	2090	3794	1420	2590	4694
1149	2100	3812	1427	2600	4712
1154	2110	3830	1432	2610	4730
1160	2120	3848	1438	2620	4748
1165	2130	3866	1443	2630	4766
1171	2140	3884	1449	2640	4784
1176	2150	3902	1454	2650	4802
1182	2160	3920	1460	2660	4820
1187	2170	3938	1465	2670	4838
1193	2180	3956	1471	2680	4856
1198	2190	3974	1476	2690	4874
1204	2200	3992	1483	2700	4892
1209	2210	4010	1488	2710	4910
1215	2220	4028	1494	2720	4928
1220	2230	4046	1499	2730	4946
1226	2240	4064	1505	2740	4964
1231	2250	4082	1510	2750	4982
1237	2260	4100	1516	2760	5000
1242	2270	4118	1521	2770	5018
1248	2280	4136	1527	2780	5036
1253	2290	4154	1532	2790	5054
1259	2300	4172	1538	2800	5072
1264	2310	4190	1543	2810	5090
1270	2320	4208	1549	2820	5108
1275	2330	4226	1554	2830	5126
1281	2340	4244	1560	2840	5144
1286	2350	4262	1565	2850	5162
1292	2360	4280	1571	2860	5180
1297	2370	4298	1576	2870	5198
1303	2380	4316	1582	2880	5216
1308	2390	4334	1587	2890	5234
1315	2400	4352	1593	2900	5252
1320	2410	4370	1598	2910	5270
1326	2420	4388	1604	2920	5288
1331	2430	4406	1609	2930	5306
1337	2440	4424	1615	2940	5324
1342	2450	4442	1620	2950	5342
1348	2460	4460	1626	2960	5360
1353	2470	4478	1631	2970	5378
1359	2480	4496	1637	2980	5396
1364	2490	4514	1642	2990	5414
			1449	3000	5432

NOTE:—The numbers in RED INK refer to the temperature either in degrees Centigrade or Fahrenheit which it is desired to convert into the other scale. If converting from Fahrenheit degrees to Centigrade degrees the equivatent temperature will be found in the left column, while if converting from degrees Centigrade to degrees Fahrenheit, the answer will be found in the column on the right.

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GEO. W. ROCKLEIN JR.

THE METALLOGRAPHY AND HEAT TREATMENT OF IRON AND STEEL

BY

ALBERT SAUVEUR, Sc.D.

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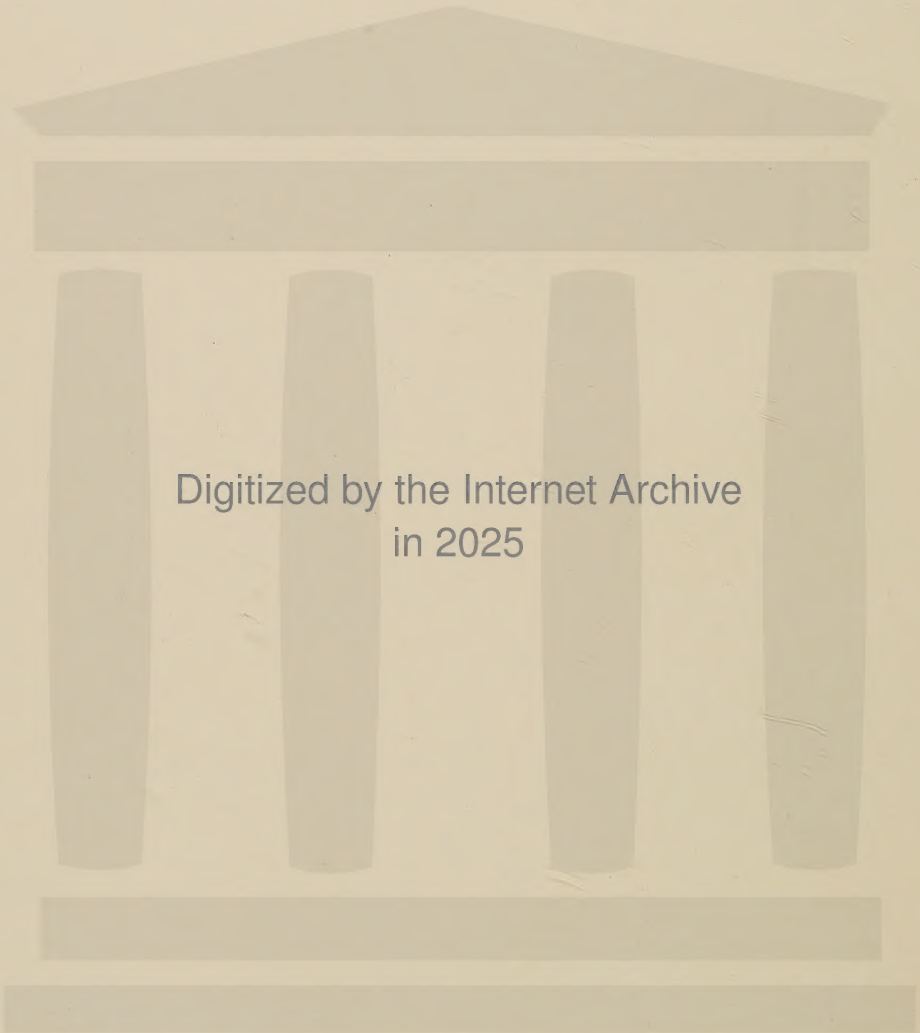
TO
THE MEMORY OF
My Father
I REVERENTLY AND LOVINGLY
DEDICATE THIS BOOK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PREFACE TO THE FIRST EDITION

While several excellent books on metallography have been published and while numerous papers on the metallography of iron and steel have appeared in the scientific and technical press, a well-balanced, specific, and comprehensive treatise on the subject has not heretofore been written. In the belief that there is a real and urgent need of such a treatise the author has endeavored to supply it, craving for his effort the indulgent criticism of his readers. He offers his book to those seeking self-instruction in the metallography of iron and steel, their special needs having been carefully considered in the arrangement of the lessons; he offers it to teachers and students trusting that they will find it valuable and suggestive as a text-book; he offers it to manufacturers and users of iron and steel in the belief that he has given due weight to the practical side of the subject and has avoided discussions of ill-founded or purely speculative theories; he offers it to the general reader interested in the scientific or practical features of the metallography of iron and steel, as the language used should be readily understood by those lacking specialized knowledge of the subject; he offers it to experts in the hope that they will find it not entirely devoid of original thought, original treatment, and suggestiveness.

In the matter of illustrations and especially of photomicrographs the author's aim has been to utilize the best available, using his own or those taken in his laboratory only when no better ones have, to his knowledge, been published by others. The original source of every illustration has been indicated and the author desires to express his indebtedness to the following writers, the figures in parentheses showing the number of illustrations from each: Andrews (3), Arnold (7), Bayley (1), Belaiew (5), Brearley (2), Carpenter and Keeling (1), Sherard Cowper-Coles (1), Desch (4), Edwards (2), Ewing and Rosenhain (2), Guillet (18), Gœrens (9), Gulliver (2), Hall (1), Houghton (1), Kroll (1), Law (8), Levy (1), Longmuir (2), Matweieff (1), Maurer (1), Mellor (1), Osmond (17), Roberts-Austen (1), Robin (1), Roland-Gosselin (1), Rosenhain (2), Saladin (2), Sorby (1), Stead (13), Tschermak (3), Tschernoff (1), Wüst (5), Ziegler (1). All illustrations not otherwise inscribed are the author's.

The author cannot refrain from expressing here the sorrow and sense of personal loss he experienced when the news was received, while this book was passing through the press, of the death of Floris Osmond, for to the author, as no doubt to many others, Osmond's work and Osmond's life have been an inspiration. Osmond belonged to that admirable class of French scientists who, like Pasteur and Berthelot, have so lofty a conception of the duty of the scientist that they give to the world the fruit of their genius and of their untiring labors with no thought of monetary return or even

of honorary recognition. If Sorby was the pioneer of metallography and Tschernoff its father, Osmond has been its torch-bearer, for he, more than any other, has been our guide. While he is no longer with us, his light will long continue to burn and to show the way to promising and productive fields of research.

The author desires to place on record his warm appreciation of the assistance he received from Mr. H. M. Boylston in passing this book through the press, and also for many valuable suggestions.

Albert Sauveur.

Harvard University,
Cambridge, Massachusetts,
August 19, 1912.

PREFACE TO THE SECOND EDITION

The sale in less than three years of two impressions of the first edition of this book justifies the author's belief expressed at the time that there was a need in the educational and industrial world of a treatise on the metallography of iron and steel such as he has endeavored to supply. Dealing with a science so young, and therefore not in full growth, it was to be expected that even after so short a period as three years there would be need of a revised edition that recent progress might be put on record and a more faithful picture offered of its present status. The necessary revisions and additions have been made to the best of the author's ability. Nearly every chapter has been revised, while some fifty pages of new text have been added and nearly one hundred new illustrations used. With the exception of the last sixty-four pages, the book has been entirely reset. In view of the fact that so large a portion of this work is devoted to the study of the heat treatment of iron and steel, the new title, namely, "The Metallography and Heat Treatment of Iron and Steel," appears to be more accurately descriptive of its contents.

In the present edition, the author has continued to follow the course previously adopted by him, to utilize the best illustrations available rather than to use his own to the exclusion of others. Too many books purporting to be treatises on certain subjects are merely expositions of the author's views to the belittling of the opinions and work of others. Authors of treatises should be just and impartial and should not give undue prominence to their own views and opinions. This, obviously, they owe to their readers and to the public in general. The author of this book hopes that he has succeeded in adhering faithfully to that belief and, if he has failed in ever so small a degree, it has been unintentional.

Of the 338 illustrations reproduced exclusive of illustrations of apparatus, 80 were prepared by the author himself, 82 by others in his laboratory, and 25 by correspondence course students. The author records here his indebtedness to the following gentlemen for illustrations borrowed from them, the figures in parentheses indicating the number in each case: Messrs. Andrews (2), Arnold (5), Bayley (1), Belaiew (5), Benedicks (2), Brearley (2), Carpenter and Keeling (2), Chappell (1), Coe (1), Sherard Cowper-Coles (1), Desch (7), Edwards (1), Ewing and Rosenhain (2), Franklin (4), Gœrens (8), Guillet (16), Gulliver (3), Houghton (1), Law (7), Levy (1), Longmuir (2), Mauer (1), Mellor (1), Osmond (20), Peirce (4), Pulsifer (1), Roberts-Austen (3), Robin (1), Roland-Gosselin (1), Rosenhain (7), Roozeboom (1), Ruff (1), Saladin (2), Sorby (1), Stead (19), Tschermak (3), Tschernoff (1), Upton (1), Wittorff (1), Wüst (3), Ziegler (1).

He also takes this opportunity of expressing his appreciation of the many kind and helpful criticisms and suggestions received from fellow-workers and other correspondents.

The method which the author has always followed in his teaching of metallography to postpone until the closing chapters the study of the equilibrium diagram and of the phase rule rather than to introduce the subject with these complex, and, therefore, at the time, forbidding, considerations has been adversely criticized by a few, but on the whole he believes that it has won out and he is more convinced than ever that it is the most effective and otherwise satisfactory method to follow.

ALBERT SAUVEUR.

HARVARD UNIVERSITY,
CAMBRIDGE, MASSACHUSETTS,
November 17, 1915.

PREFACE TO THE THIRD EDITION

The author is deeply appreciative of the kind and indulgent reception accorded the first two editions of his book and of the wishes expressed by many for a third revised edition. Fully conscious of his responsibility and of the expectations of his readers, he has attempted, to the best of his ability, to incorporate in the present edition the advance recorded in the metallography of iron and steel during the last decade. He has adhered to the policy adopted by him from the start not to include lengthy descriptions of controversial matters or of speculative theories. His book is written primarily for those who seek instruction based on the soundest foundations the science of metallography affords. He has also refrained from giving to his personal views greater prominence than to those expressed by authoritative investigators. As he grows older, he becomes ever more conscious of the frailty of human knowledge, of the vastness of what one does not know, of the folly of dogmatism!

Corrections of erroneous statements and constructive criticism will be gratefully received.

Albert Sauveur.

Harvard University,
Cambridge, Massachusetts,
March 27, 1926.

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CHAPTER I

PURE METALS

Metals as used in the arts are never chemically pure. Indeed they frequently contain very notable quantities of impurities. It has often been attempted to produce absolutely pure metals that their properties might be determined and studied. In these attempts the aim has been generally to eliminate to the greatest possible extent the impurities usually contaminating them or to prevent such contamination from taking place. In some instances, great, if not actual, purity has been obtained so far as the absence of the impurities commonly present is concerned. While seeking purity, however, the possible existence of gases is often overlooked, with the result that many supposedly pure metals, obtained by fusion in free contact with air, frequently contain gases, for it is well known that molten metals under these conditions will absorb readily such gases as hydrogen, nitrogen, and oxygen, and that a portion of them at least will be retained in the solidified metal at room temperature. The gases thus retained are generally known as "occluded" gases. They probably form solid solutions with the metal, either by being dissolved as such, or by first forming with a portion of the metal a definite compound, an oxide in the case of oxygen, which is then dissolved. The marked influence which even small quantities of gases may have on some of the physical properties of otherwise pure metals has been repeatedly shown.

Obviously to secure metals free from gases they should be melted in vacuo, but even with the most perfect vacuum obtainable, it is doubtful whether the occluded gases can be completely eliminated.

On the other hand, if the metals have been obtained by electrolytic deposition they necessarily contain hydrogen, which subsequent remelting in vacuo may fail to expel completely. If these views are correct, it follows that the production of strictly pure metals is well-nigh an impossible feat, and consequently that our knowledge of their properties may be quite deficient.

With these reservations in mind the solidification, crystallization, and structure of "pure" metals may be considered.

Crystallization. — When a substance passes from the liquid to the solid state, the process of solidification is generally accompanied by crystallization, i.e. the atoms or molecules of the substance so arrange themselves as to form small solids of regular geometrical outlines, such as cubes, octahedra, etc. Each of these *spontaneously* formed symmetrical solids is called a crystal and any substance made up of crystals is said to be crystalline.

Solid substances which are not crystalline are said to be "amorphous." They are characterized by the absence of any symmetrical grouping of their atoms or molecules. Pitch is a good example of an amorphous substance.

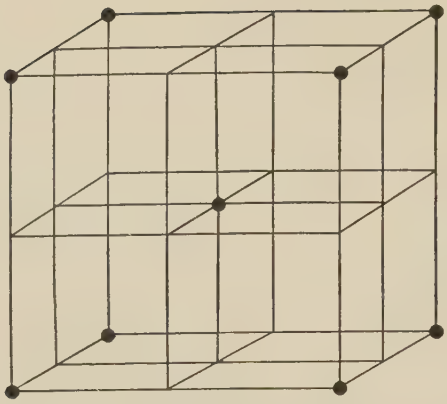


Fig. 1. — Body-centered cubic arrangement of atoms. (Hull.)

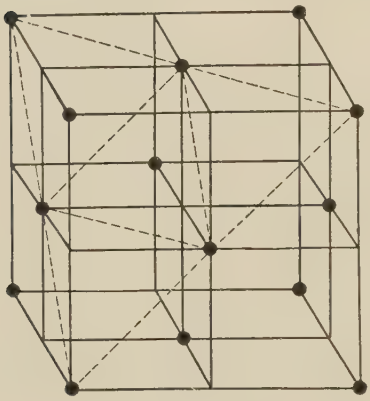


Fig. 2. — Face-centered cubic arrangement of atoms. (Hull.)

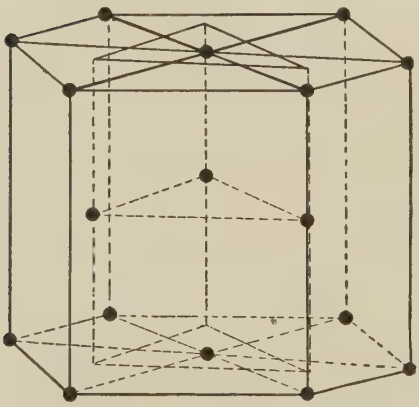


Fig. 3. — Hexagonal close-packed arrangement of atoms. (Hull.)

Atomic Structure of Crystals. — The study of the atomic structure of crystals by means of the diffraction of X-rays has made much progress in recent years. For a brief description of the method the reader is referred to "The Science of Metals" by Jeffries and Archer, pages 51 et seq. It has been found that in most metals the atoms form "body-centered" or "face-centered" crystals, in a few hexagonal, close-packed crystals. In body-centered lattices the atoms occupy the eight corners of a cube, while one atom is situated at the center (Fig. 1); in face-centered lattices there is no atom at the center but the center of each of the six faces of the cube is occupied by an atom (Fig. 2); in hexagonal close-packed lattices an atom is found at each prism corner and at alternate prism centers (Fig. 3). The face-centered and hexagonal arrangements represent a closer packing of atoms than the body-centered arrangement.

All malleable and ductile metals such as gold, silver, platinum, copper, aluminum, and nickel have face-centered cubic lattices. Gamma iron, that is iron above the A_3 point (900° C.±), also has a face-centered lattice and we know it to be ductile. Alpha iron, however, or ferrite, which is the condition of iron at room temperature, although very ductile, has a body-centered lattice which is generally exhibited by non-ductile metals such as chromium, molybdenum, tungsten, titanium, etc. Bismuth, magnesium, titanium, zinc, and zirconium have hexagonal close-packed lattices.

The following is quoted from Jeffries and Archer ("The Science of Metals," page 61):

"1. No metal crystallizing with the face-centered cubic arrangement has been found so far which is not ductile throughout a considerable range of temperature. The face-centered metals are usually ductile even at liquid air temperatures.

"2. All of the noble metals so far studied crystallize with the face-centered cubic arrangement.

"3. All of the best electrical and heat conductors have face-centered cubic arrangements.

"4. Both ductile and brittle metals are found in the body-centered cubic arrangement. This system seems to be less favorable to ductility than the face-centered, according to Hull.

"5. In the hexagonal arrangement, both brittle and ductile metals are found. Hull points out that in the hexagonal arrangement there is only one set of planes parallel to which easy gliding can take place, whereas in the face-centered cubic there are four.

"6. Metals having the hexagonal close-packed arrangement harden rapidly under cold deformation.

"7. Mechanical twinning (Neumann lines) occurs in metals having the centered cubic and the hexagonal close-packed arrangements. Alpha iron is an example of the former and zinc of the latter. Mechanical twins have also been observed in tin, which is thought to crystallize in the tetragonal system.

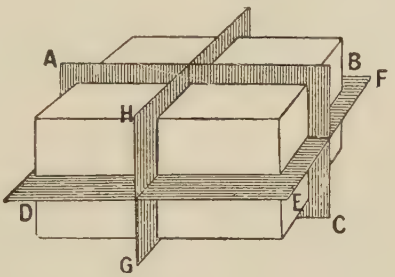


Fig. 4. — Cleavage planes. (Mellor.)

"8. Annealing twins are certainly most prevalent in metals crystallizing in the face-centered cubic arrangement.

"9. Annealing twins have not been observed in metals having the body-centered cubic arrangement, such as alpha iron, tungsten, and molybdenum.

"10. Not all face-centered metals show twinning. Twin crystals have not been observed in aluminum, for example."

This new method of investigation seems destined to become of great scientific importance. What it will do for metallurgy is difficult to foretell. Practically its only contribution to date, to ferrous-metallurgy at least, has been to show that alpha and beta iron have the same space lattices and hence, according to some, cannot be allotropically different, and that martensite, the constituent of hardened steel, contains chiefly alpha iron. It will be explained later, however, that it was already known that no difference existed in the crystallography of alpha and beta iron and that many believed the iron in martensite to be present in the alpha condition. Ingenious speculations based on the results of X-ray analysis in regard to the atomic structure and properties of solid solutions may in time develop into useful hypotheses to be used as tools in our scientific advance toward a goal which must of necessity rescind as we approach it but which nevertheless brings its reward. Let not the glamour and attractiveness of a new theory, however, dim our vision lest we lose our sense of proportion, as many did when the phase rule was first applied to metallurgical problems.

Cleavage. — Crystals possess the property of breaking more readily in one or more directions. This property is called "cleavage." The planes of cleavage or directions of easy rupture are generally parallel to the faces of the crystals. A cubic crystal, for instance, splits readily along three planes parallel to the three sets of faces

of the solid. In Figure 4, ABC, DEF, and GHI indicate the cleavage planes of a cubic crystal. The direction of its cleavage planes constitutes the orientation of the crystal.

Idiomorphic Crystals. — When the fluidity of a substance and other conditions are such that the formation and growth of the crystals are given free play, perfect (and sometimes very large) crystals are produced. These perfect crystals, with faultless geometrical outlines, perfect cubes for instance, are called "idiomorphic" crystals.

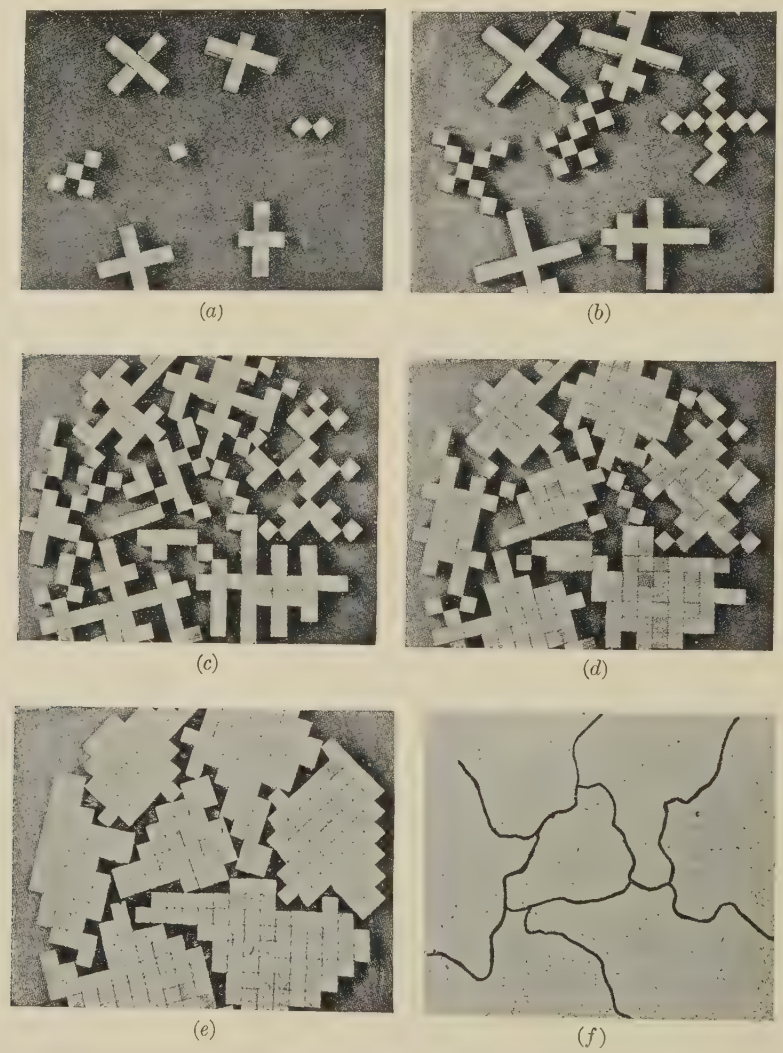


Fig. 5. — Illustrating the growth of crystalline grains. (Rosenhain.)

Allotriomorphic Crystals. — When the free development of crystals is hindered by less favorable crystallizing conditions, such for instance as contact with other crystals, likewise in process of formation, the regular external form is not preserved and the resulting imperfect crystals are called "allotriomorphic" crystals, also, but more seldom, "anhedrons" or faceless crystals. Such crystals are said to have taken their shape from their surroundings. It should be noted, however, that allotriomorphic

crystals, like idiomorphic crystals, are composed of crystalline matter. An allotriomorphic crystal may be regarded as resulting from the mutilation of an idiomorphic crystal, the mutilation affecting the external shape only, and not the crystalline character of the substance.[1]

Crystallization of Metals. — Metals when they solidify generally give rise to the formation of allotriomorphic crystals. The explanation for this is to be found in the fact that crystallization sets in simultaneously at many centers. From each center a crystal grows through successive additions of crystalline matter similarly oriented, until meeting with other surrounding crystalline growths, radiating from other centers, the free development of its external form is arrested. The mechanism of this crystalline growth has been clearly illustrated by Rosenhain (Fig. 5). Five stages of the progressive growth of the grains are shown in *a* to *e*, while in *f* the final polygonal out-

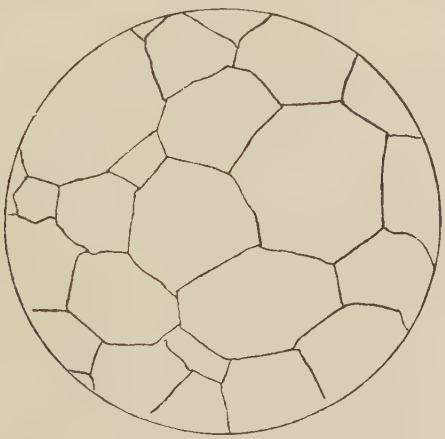


Fig. 6. — Pure gold magnified 50 diameters.
(Andrews.)

line of the grains is indicated. The polygonal networks shown in Figures 6 and 7, representing respectively the structure of pure gold and pure copper, do not indicate, therefore, outlines of true crystals, but merely boundaries or junction lines between adjacent crystalline growths or "grains." They mark the regions where neighboring crystalline growths met with resulting distortion of their external forms. Some believe, as explained later, that a little amorphous metal is left at the boundaries.

The number of crystalline grains of which a certain mass of metal is composed must depend, therefore, upon the number of centers or nuclei at which crystallization begins, and this in turn probably depends upon the metal itself, the temperature at which it is cast, its rate of cooling, and, according to some, its purity; the slower its solidification and the greater its purity the fewer the nuclei and therefore the larger the crystalline grains.

Granular or Polyhedral Structure of Metals. — When a properly prepared sample of a pure metal in the cast condition is examined under the microscope, the revealed structure generally presents the appearance of a polygonal network (Fig. 6), an indication that the metal itself is composed of irregular polyhedral grains, each mesh or

[1] Crystalline groups or aggregates of allotriomorphic crystals are sometimes called "crystallites," while if they assume some distinct form they may be further described as "dendrites" or "tree-like," "pine-tree," "fern-leaf," "star-like crystallites," "crystalline grains," etc.

polygon of the network representing a section through a polyhedron.[1] The allotriomorphic crystals formed when metals solidify are called generally by metallurgists "crystal grains," "crystalline grains," or even simply "grains." The expression crystalline grains, which is quite common, appears satisfactory since it suggests the two main facts to be remembered as to the nature of the grains, — (1) that they are not perfect crystals and (2) that they are nevertheless crystalline. Dana himself writes that cast iron is made up of *crystalline* grains. He says further: "Crystallization produces masses made of crystalline grains when it cannot make distinct crystals." Nor is there very great objection if, for the sake of brevity, the word grain alone be used, bearing in mind once for all the crystalline character of metals.

To render the polygonal boundaries of crystalline grains visible under the microscope the highly polished metallic surface must generally be treated by an acid or

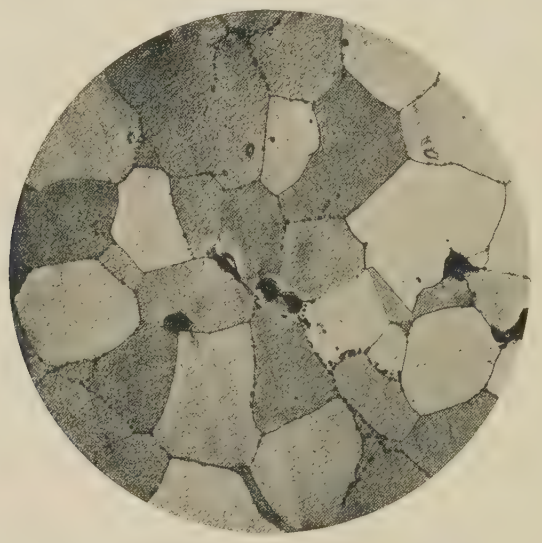


Fig. 7. — Pure copper. Magnified 125 diameters.
(F. C. Langenberg, in the author's laboratory.)

some other chemical reagent capable of dissolving or corroding the metal, with or without deposition of a film of some precipitated matter. According to Ewing these boundaries are made evident by the differential action of the acid, which produces differences of level by attacking one grain more energetically than its neighbors. Each of the short sloping surfaces which connect one grain with another appears black under vertical illumination because it does not reflect the light back into the tube of the microscope.

Another explanation of the nature of these boundaries will be discussed later.

Crystalline Orientation of the Grains. — A slight chemical attack or etching of the polished samples brings out merely the polygonal structure described and illustrated in the preceding pages. If the etching be somewhat deeper, however (through the use of a stronger reagent or because of a longer attack), it is observed that the polygons or meshes of the network are differently colored (Fig. 7), some appearing

[1] Homogeneous solid solutions and, frequently, definite compounds also assume polyhedral structures, this type of structure being characteristic of the existence of but one phase. (See Chapter XXIV).

very dark, others less dark, others still, brilliant. This heterogeneousness in the appearance of sections through adjacent grains is due to the fact elucidated above, that *each grain, i.e. each allotriomorphic crystal, is made up of crystalline matter similarly oriented in the same grain but differently in different grains.* Bearing this in mind, the dissimilarity of coloration between contiguous grains is readily explained, for if the crystalline matter of any individual grain is so oriented that it reflects the incident light into the microscope-tube, that grain will appear bright, while, on the contrary, if its orientation is such that the light is reflected outside the microscope, the corresponding grain will appear dark. By slightly inclining the sample in various directions, or by rotating it, some of the grains that were bright become dark, being, so to speak, extinguished, while some of the dark grains become brightly illuminated, because in so doing we change the direction of the light reflected by each individual grain section. Similar results are obtained by changing the direction of the incident

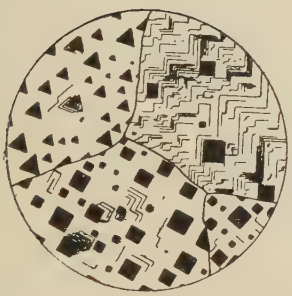


Fig. 8. — Typical etching figures of pure metals. (Gulliver.)

Fig. 9. — Part of a crystalline grain of bismuth. Magnified 5 diameters. (Gulliver.)

light. The kaleidoscopic effect just described affords a conclusive proof of the crystalline nature of metals and of the correctness of the explanation offered to account for the dissimilar appearance, as to tint, of contiguous grains.

Cubic Crystallization of Metals — Etching Pits. — By still deeper etching of the polished surfaces of pure metals, it is sometimes possible to bring out clearly the crystalline character of the individual grains (see Fig. 8). The figures thus outlined, in reality small cavities, are often called "etching pits" or "etching figures." These figures frequently correspond to sections of cubes or of geometrical solids derived from the cube, indicating that most metals crystallize in the cubic system (also called regular, or isometric, or monometric system).[1]

In Figure 9 is seen after Gulliver part of a single grain of bismuth. It is clearly made up of small crystals of geometric form.

Summary. — Summing up the indications obtained by the microscopical exam-

[1] The other crystallographic systems are the hexagonal, the tetragonal, the orthorhombic, the monoclinic, and the triclinic.

ination of polished and etched surfaces of pure metals, it has been shown (1) that a slight etching outlines the polygonal boundaries of adjacent crystalline grains, (2) that a deeper etching imparts different colorations to the various polygons or grain sections, a phenomenon which is due to the constancy of crystalline orientation in any individual grain and to the change of orientation as we pass from one grain to the next, and (3) that a still deeper attack often brings out clearly pits of distinct geometrical forms, often cubic, indicating that the majority of metals crystallize in the cubic system.[1]

The Amorphous Cement Theory and the Boundaries of Crystalline Grains. — According to Rosenhain and Ewen the boundaries between adjacent grains are not merely surfaces of contact but narrow spaces filled with amorphous metal or cement holding the grains together. This hypothesis is an extension of Beilby's theory of the existence of an amorphous state in metals caused by mechanical straining as outlined elsewhere. The authors argue that if the various crystalline grains were merely held together by surface contact the boundaries should be weaker than the mass, whereas on the contrary fractures generally occur through the crystalline grains instead of following their outlines. Howe, however, pertinently asked why, following this reasoning, the surfaces of contact between the grains and the surrounding amorphous cement membranes should not be as many planes of weakness which the fractures should follow. In other words, why should the contact between a crystalline mass and an amorphous mass of the same metal form a stronger union than contact between two crystalline masses of that metal? His question has never been answered.

Rosenhain writes: "Where the constituent crystals of a metal meet, thin films of residual liquid will remain under conditions rendering them incapable of crystallizing so that they constitute thin films of undercooled[2] liquid or amorphous metal acting as intercrystalline cement . . . When two differently oriented crystals meet, there must be a region between the two orientations, where the material cannot assume the orientation of either . . . The fundamental fact is the marked strength of crystal boundaries in pure metals."

The formation of amorphous films between two crystalline grains is graphically represented, according to Rosenhain, in Figure 10. *A* and *B* are sections through two adjacent grains, while the shaded portion between them represents the residual liquid which remains amorphous on solidifying. F. C. Thompson explains plausibly the existence of amorphous films between the grains as due to opposing orienting forces emanating from two crystals neutralizing each other. The same writer further contends that the amorphous films surrounding the crystalline grains are not inherently hard and non-ductile but owe their hardening effect to the action of surface tensions at the boundaries between amorphous cement and crystalline matter.

The existence of amorphous crystalline cement is offered as an explanation for the greater strength and toughness of a fine-grained structure, seeing that it must contain a greater quantity of strong amorphous cement. Howe writes: "This greater

[1] We have other indications of the cubic crystallization of metals, such for instance as the space lattices revealed by X-ray analysis and the hexagonal character of many of the polygons which crystallographers consider to be due to interfering cubes and octahedra (the octahedron is a form belonging to the cubic system). Again, under favorable crystallizing conditions nearly perfect cubes have been obtained in the case of several metals.

[2] The undercooling of a substance means its cooling to a temperature lower than that at which a certain transformation should normally take place without inducing that transformation. Water, for instance, cooled below its freezing point without causing the formation of ice is in an undercooled condition, or, to express it differently, it is in "metastable" or "labile" equilibrium. (Chapter XXVI).

strength is natural, because the amorphous state lacks the cleavages and slip planes which weaken crystalline substances." It will be shown also that the theory affords an explanation of the alteration of many of the properties of pure metals when subjected to thermal and mechanical treatments.

Obviously if the metal exhibiting these amorphous cement membranes is strictly chemically pure, the cement, as well as the crystalline matter, are both of the same degree of purity; but it is well to bear in mind that, as previously mentioned, metals supposed to be pure may contain appreciable quantities of impurities, notably of gases which chemical analysis may have failed to reveal or for which no search was made. These unsuspected or ignored impurities may segregate in the amorphous cement rather than in the crystalline grains, due to the mechanism of solidification later to be described. Whenever impurities are present, therefore, it may be assumed that the amorphous phase is more impure than the crystalline phase. Indeed,

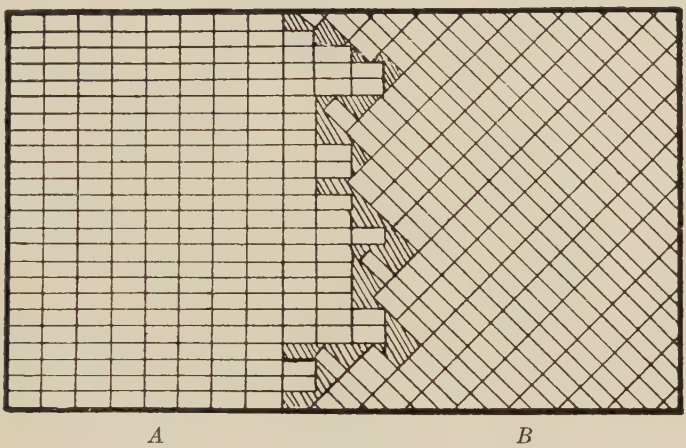


Fig. 10. — Section through two adjacent crystalline grains. (Rosenhain.)

some believe that the segregation of impurities is sufficient to account for the boundaries around the crystalline grains on the ground that really pure metals do not exist. They argue that the boundaries consist of impurities thrown off on solidifying.

Professor W. D. Bancroft rejects the amorphous film theory on the ground that its advocates "have taken whatever properties they needed and have assigned them arbitrarily to the hypothetical amorphous phase." He asks us to assign those properties arbitrarily also, it would seem, to small crystals. Few, it is believed, will be convinced by his argument. The colloid chemist still has to win his spurs in metallurgy.

The difference between Beilby's and Rosenhain's amorphous cements should not be overlooked: the former results from the severe straining of crystallized metal, the latter from the solidification of liquid layers enclosed in such narrow spaces that they cannot assume a crystalline orientation. From the well-supported contention, therefore, that Beilby's cement exists and that it is strong, hard, and brittle, it does not necessarily follow that Rosenhain's cement possesses similar properties or indeed that it exists at all.

Attractive as this amorphous theory is, and notwithstanding the ability with which it has been presented and the renown of its sponsors and supporters, it should not be accepted without reservation as a demonstrated fact but, as Professor Howe

writes, as "a precious working theory rather than a firmly established one." So long as it explains more satisfactorily than other theories a greater number of phenomena in which it may play a part we should use it in preference to others as the best available tool. Let us avoid the danger, however, into which too many fall, of accepting as indisputable truth, statements and theories emanating from those whom we hold in great esteem. It is not what these men themselves should wish us to do.

Polished pieces of steel as well as severely cold worked steel have been subjected to X-ray analysis, and it has been reported that the diffraction patterns obtained are not different from those yielded by the same steel before cold working or polishing. Some infer from this that no amorphous metal can result from polishing or cold working on the ground that if it existed in the samples tested it would affect the X-ray pattern. See addendum at end of chapter.

Isotropism and Anisotropism. — A crystal, because of the constancy of orientation of the crystalline particles of which it is composed, does not possess identical proper-

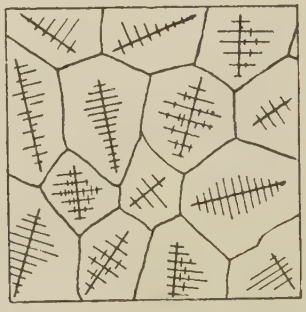


Fig. 11. — Dendritic crystallization. (Desch.)

ties in all directions: it is anisotropic. A crystalline mass, however, made up of numerous anisotropic crystalline grains may be considered isotropic, that is, having like properties in all directions, on the ground that the variation of properties of individual grains neutralize each other, unless indeed "directional" properties have been imparted to it by mechanical deformation or other causes, as later explained. To quote Portevin, "Metals are pseudo-isotropic aggregates of anisotropic elements."

Dendritic Structure. — While generally, under the microscope, the network structure just described is the only one to be observed, it is highly probable, for reasons later to be offered, that the solidification of pure metals gives rise to the formation of dendrites or pine-tree crystallites. The relation existing between this dendritic crystallization and the polyhedral structure should be considered. It may be assumed with Desch and others that this relation is correctly represented in Figure 11. This would indicate that each crystalline grain results from the gradual growth of one dendrite, itself composed of small cubic or octahedral crystals similarly oriented. It is hardly to be assumed that any grain may contain more than one dendrite since two or more dendrites could not belong to the same grain unless they had identical crystalline orientation, which in turn would cause them to lose their identity.

The usual etching treatments by which the polyhedral or granular structure of pure metals is readily revealed fail, however, to disclose the dendritic character of the grains. A reason for this should be sought. It will be shown later that some impure

metals as well as many metallic alloys, namely those forming solid solutions, are likewise constituted after solidification of dendritic crystals and that it is often possible through the use of suitable reagents to disclose their dendritic structure. Applied to pure metals, however, these special reagents fail to reveal the presence of the dendrites. It is not on record, so far as I know, that the dendritic structure of the grains of chemically pure metals has ever been disclosed by etching methods. The failure of etching reagents to reveal the dendrites of pure metals is readily explained if we bear in mind that the patterns produced by their use is necessarily due to selective action, the reagents affecting some portions of the surface to the exclusion of others or in a different degree or manner. This in turn implies heterogeneity, chemical or physical, of the surface under examination. By chemical heterogeneity is meant here, differences in composition between various portions of the surface examined,

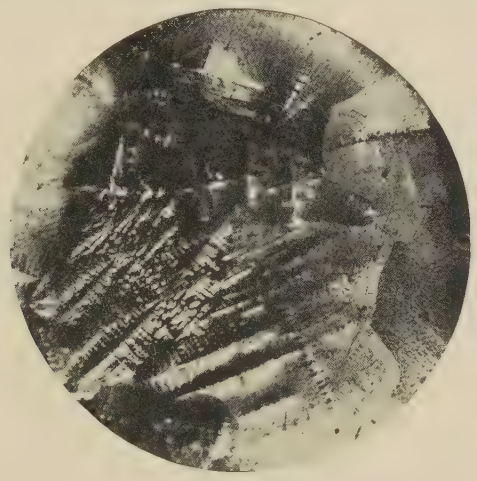


Fig. 12. — Dendrites on surface of cast copper. Magnified 2 diameters. (E. L. Reed, in the author's laboratory.)

while physical heterogeneity implies the presence of both amorphous and crystalline phases of the same matter, or simply differences of orientation of the crystalline phase. In the case of pure metals, however, this heterogeneity is lacking, each portion of a dendrite having necessarily the same composition as any other portion, as well as the same crystalline orientation. Under these conditions the selective action of the reagent cannot be exerted and the structure remains hidden. Were it not for the fact that adjacent grains have unlike orientation, or possibly for the existence of amorphous metal at their boundaries, their existence could not be disclosed by etching treatment. The heterogeneity necessary for the effective application of etching methods exists between the various grains of pure metals as well as between the grains and their boundaries, but is absent *in the grains themselves*, hence the possibility of revealing the existence of these grains by such methods and the failure of disclosing their internal structure. While thus recognizing the impossibility of bringing out the dendritic structure of pure metals by etching methods it should be borne in mind, as mentioned at the beginning of this chapter, that strictly pure metals hardly exist and that the presence of but a small quantity of gas may supply the heterogeneity of composition needed for the detection of that structure. There is little doubt but that the

possibility of bringing out the dendritic structure would be an indication of the presence of impurities. As later to be explained it implies segregation, and there is no segregation possible in the complete absence of impurities. From this apparent impossibility to bring out the dendritic structure of pure metals the conclusion that such structure does not exist would be unwarranted. Indeed every sound consideration points to its existence. Dendrites, for instance, are frequently observed on the cooling surfaces of pure metals or in internal cavities, under crystallizing conditions permitting their unhindered formation (Fig. 12).

It will be shown at the proper time that the dendritic structure of impure metals and of some metallic alloys is frequently on so large a scale that it can readily be observed with the naked eye, that is, their dendritic structure is "macroscopic" and not microscopic. In the case of pure metals, however, the polyhedral structure is nearly always microscopic, and if the relation that structure bears to the unrevealed

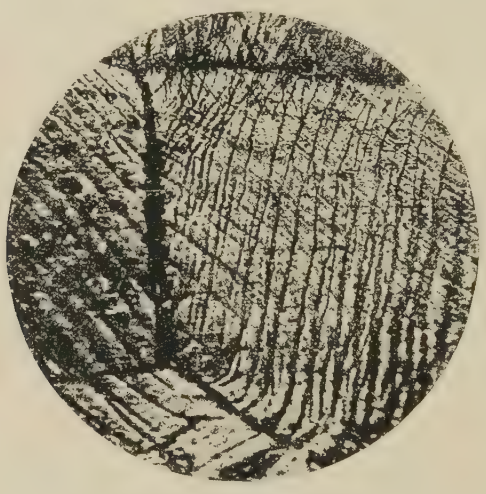


Fig. 13. — Slip bands in Swedish iron strained by tension. Magnified 400 diameters. (Ewing and Rosenhain.)

dendritic structure has been correctly interpreted in these pages (Fig. 11), it necessarily follows that the latter should be *a fortiori* microscopic. The possibility, however, of the coexistence of micrograins and macro-dendrites in impure metals and alloys will soon be considered, as well as the possibility of macro-dendrites and macrograins of pure metals breaking up into micrograins on cooling below the solidification temperature. The formation of dendrites is considered at greater length in the following chapters.

Influence of Mechanical Treatment. — Metals are frequently subjected to powerful pressure exerted by rolls, presses, hammers, etc., with a view of producing metallic objects of desired shapes. This treatment affects the structure, and therefore the properties of the metal. Roughly speaking, such vigorous kneading has a tendency to reduce the size of the final grains, either through preventing the formation of large grains or by breaking up or distorting preëxisting grains. A smaller grain, in turn, generally implies greater ductility (provided it be not distorted), and often greater strength. If the work is performed at low temperature (cold working), it generally results in severe and permanent deformation of the crystalline grains, and this in turn

produces marked increase of tenacity, elastic limit and hardness, but greatly reduces the ductility, causing eventual brittleness of otherwise very ductile metals. Ductility may be restored by annealing.

Straining of Metals — Slip Bands. — Ewing and, later, Ewing and Rosenhain through some skillfully conducted experiments and convincing reasoning have revealed the character of the strain produced in a pure metal by the action of a stress which may eventually cause its rupture.

Polished sheets of metals were strained very gradually while being examined under the microscope. When the yield point is reached, i.e. when plastic deformation begins to occur, black lines are seen to cross the crystalline grains of which the metal is made up. These lines are generally quite straight and are parallel in the same grains but have different directions in different grains. Figure 13 shows the appearance under vertical light of Swedish iron strained by tension, magnified 400 diameters.

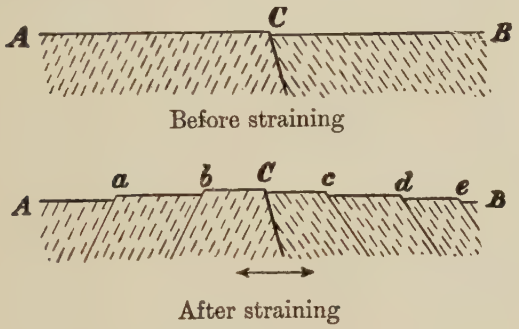


Fig. 14. — Diagram illustrating the effect of strain upon the structure of metals and alloys. (Ewing and Rosenhain.)

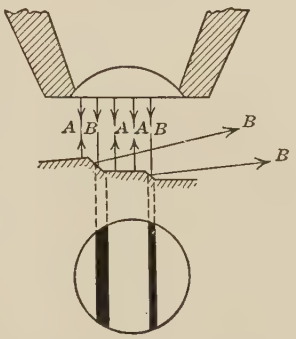


Fig. 15. — Sketch showing why slip bands appear dark. (Rosenhain.)

As the strain increases, other systems of lines, inclined to the first, make their appearance and eventually two, three, and even four systems of intersecting lines may be seen in each grain.

These lines are not cracks but steps in the surface, which steps are due to slips along the cleavage or gliding planes of the crystals.[1] In Figure 14, AB represents the polished surface of two grains, C the junction line between these two grains. The pull takes place in the direction of the arrows.

Yielding occurs by finite amounts of slips at a limited number of places, *a*, *b*, *c*, *d*, *e*, resulting in short portions of inclined cleavage or sliding surface appearing black under the microscope, because they do not send back any light into the tube. By oblique light some of these slip bands appear black while others are bright. When the surface is rotated some of the bands which were black become bright and vice versa, owing to the change of their position in regard to the incidence of the light, which is conclusive proof that the black lines are not cracks, but inclined surfaces as described above. The reason why slip bands appear dark when viewed under direct illumination is clearly shown in Figure 15.

[1] According to Humfrey the crystal properties of cleavage and gliding are in many ways distinct, and do not necessarily occur with maximum readiness along the same crystallographic planes. This difference probably occurs in the case of crystals of iron, which have been shown to possess cubic cleavage planes, but octahedral gliding planes.

It is seen then that metals remain crystalline after the severest strain, and that the flow or plastic strain in metals is not a homogeneous shear such as occurs in the flow of viscous fluids, but is the result of a limited number of separate slips, the crystalline elements themselves undergoing no deformation.

The Amorphous Cement Theory and the Straining of Metals. — Beilby contends that during the polishing of metals with very fine powders thin layers of amorphous metal are produced considerably harder than the metal itself and necessarily severely strained. Osmond and Cartaud had previously made a similar observation. If it be accepted that an amorphous condition may be produced on the surface of a polished specimen through the mechanical straining of the polishing operation, it is a fairly logical conclusion that in the cold working of metals the severe straining which that operation induces will likewise produce layers of amorphous metal or cement along the gliding planes of crystals which have undergone the slipping described by Ewing and Rosenhain. The following remarks from Beilby will be helpful:

> The theory of flow and resolidification in a vitreous-amorphous state for which I am responsible . . . postulates that layers of molecules many molecules in thickness have the mobility of the liquid state conferred on them for a brief period; that it is the transient existence of this mobile phase which makes the slip and movement along the lamellæ possible and easy, and that it is the sudden resolidification of these layers into a non-crystalline or vitreous condition which arrests deformation under a given deforming stress. The original surfaces of any slip are now cemented together by the more rigid material and new surfaces of slip are only developed by higher stresses. The plasticity of the crystalline state is thus gradually used up and the aggregate as a whole becomes more and more rigid. When this has reached a certain stage further increase of stress leads, not to plastic flow, but to disruption.

Rosenhain likewise clarifies our understanding of the theory when he writes:

> Just as the rubbing action of polishing produces on metal surfaces a thin layer of altered amorphous material, so we may well expect that the sliding over one another of adjacent slip surfaces will produce a local disturbance of molecular arrangement. If the slip is slight, then it probably happens that the derangement is also slight and temporary and that the disturbed molecules are still able to rearrange themselves pretty much in their original system. If, on the other hand, the slip has been more pronounced, the resulting local disturbance will also be more far-reaching, a greater number of molecules will be disturbed, and they will no longer be able to rearrange themselves in the old crystalline system. A more or less thin layer of amorphous metal will thus be formed on each surface of slip. At first, for a short time, these layers will probably possess a certain degree of mobility, like the surface film which adjusts itself under surface tension. During this period these layers would act as a sort of lubricant, facilitating further slip on the same gliding planes. After a time, however, when the disturbed molecules have had time to "set" in the amorphous condition, we should have on each plane where slip has taken place a layer of hard, non-plastic, amorphous metal.

To the formation of this cement may be ascribed the marked changes of properties accompanying the cold working of metals, such as increased tenacity and hardness, decreased ductility and density, etc.

Humfrey having observed the behavior of slip bands in the vicinity of the grain boundaries and assuming the existence of intercrystalline cement, writes: "All the observations demonstrate the resistance to plastic deformation by slip which occurs at the crystal junctions, and suggest the idea that each crystal is surrounded by and firmly attached to a continuous skin, which, while hard and plastically undeformable, is yet thin and capable of elastic bending and stretching . . . The state of affairs can best be conceived by imagining that after overstrain each crystal is enclosed and held within a stretched skin holding it so as to oppose further strain in the same direction."

In a recent communication to the author, Dr. Rosenhain writes:

"I still think that a disorganized more or less amorphous layer is formed where slip occurs, but I do not attribute the whole of the hardening of the metal to the presence of these layers, but rather to the distortion of the space lattice of the crystals in the adjacent layers in which the lattice arrangement remains intact but is distorted out of its normal uniformity by the fact that some of the adjacent atoms are no longer in their proper position. Such a disturbance is bound to propagate itself throughout the adjacent lattice in the shape of a slight distortion or curvature of the planes, and it is probably this distortion rather than the hardness of the very thin amorphous layers themselves which produces marked changes in the properties of cold-worked metal and also the effect upon the X-ray spectrum obtained from them."

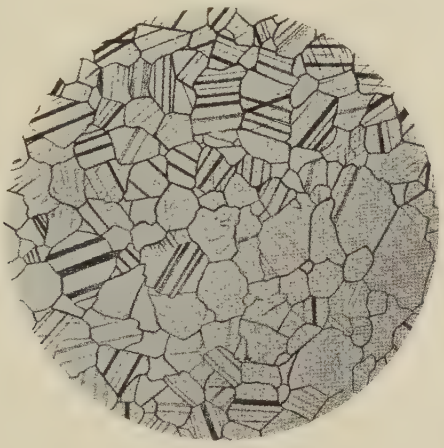


Fig. 16. — Twinnings in marble (caused by pressure). Magnified about 5 diameters. (Bayley.)

Twinning and Twin Crystals. — By twinning is meant the grouping of two or more crystals or parts of crystals in such a way that they are symmetrical to each other with respect to a plane between them (the twinning plane), which plane, however, is not a plane of symmetry. Twins result generally from a portion of a crystal turning by a definite angle, say 180 degrees. Thorne describes the formation of twins as due to the rotations of certain parts of some grains "into a position, or more exactly into an orientation, symmetrical with the initial orientation and hence with that of the remainder of that grain." Twins assume the appearance of broad bands parallel in any one grain. Being differently oriented some of these bands may appear dark while others are brilliant. They are sometimes produced by straining alone (Fig. 16), when they are called mechanical twins, but more often by straining followed by annealing (annealing twins). Many metals after such treatments contain numerous twins (Fig. 17). The production of twin crystals in the complete absence of strain is doubtful.

Neumann Bands. — The crystalline grains of metals are sometimes found to be crossed by a number of parallel lines or narrow bands (Fig. 18), called "lines or bands of Neumann," which might at first be taken for slip bands but which, according to Osmond and Cartaud and others, are undoubtedly mechanical twins. They follow the orientation of the grains. Neumann bands are generally produced by a

sudden deformation of the metal such as would result from shock, impact, or explosion. If the suddenly applied stress has caused the rupture of the metal, the Neumann bands will generally be found in close proximity to the fracture. Metals

Fig. 17. — Twinnings in copper produced by straining followed by annealing. Magnified 125 diameters. (F. C. Langenberg, in the author's laboratory.)

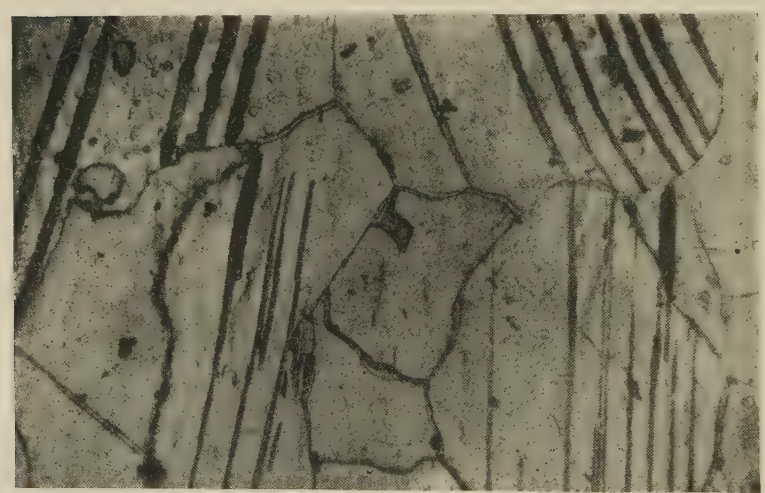


Fig. 18. — Lines of Neumann in a low carbon steel sheet. Magnified 100 diameters.

deformed or fractured by a gradually applied stress seldom if ever contain Neumann bands.

Rosenhain and J. McMinn believe that Neumann bands are sections through lamellæ or plates and not of thin rods. They further believe that they are not of the nature of mechanical twins but result from localized deformation brought about by the rapid application of a heavy stress. They report that after slowly straining a

sample of iron and causing numerous slip bands to occur on its polished surface, the subsequent sudden application of stress fails to produce Neumann bands, the additional deformation under impact taking place by further slip on some of the slip planes previously developed by the slow plastic strain. ("The Plastic Deformation of Iron and Formation of Neumann Lines," Proc. Royal Society A, Vol. 108, 1925.)

Slip Bands vs. Twins and Neumann Bands. — There may be occasionally some difficulty in distinguishing under the microscope between slip bands on the one hand and twin and Neumann bands on the other. Bearing in mind, however, that the appearance of slip bands results from differences of level within the same grain produced on polished surfaces, it is obvious that on repolishing the strained metal the slip bands should disappear while twins and Neumann bands persist.

Referring to the disappearance of slip bands on repolishing a strained specimen, Rosenhain writes:[1]

"It is true of course that when slip bands have been produced on a previously polished surface and this is repolished, no traces of them remain in the ordinary way. If, however, the deformation has been very severe, as, for instance, in the vicinity of a fracture, when the surface is repolished and simply etched, traces of the old slip bands do reappear."

Rosenhain further states that slip bands are always extremely fine black lines, whereas Neumann lines and twin bands are much broader, and also that he does not think that Neumann lamellæ are of the nature of twins.

Influence of Thermal Treatment. — The size of the crystalline grains of pure metals varies in different metals even when cast and cooled under identical conditions. Their dimension is generally affected also by the rate of cooling during solidification and, therefore, by the size of the casting, since a large casting will cool more slowly than a smaller one. It is possibly affected also by the casting temperature.

It is generally held that during a slow solidification, crystallization proceeds from a relatively small number of nuclei and that the final grains therefore are large, while rapid solidifying induces crystallization from a greater number of centers, resulting in smaller grains. As previously mentioned, a fine-grained metal is generally more tenacious and harder than the same metal in a coarse-grained condition. This is explained by the amorphous cement theory on the ground that the former contains necessarily more of the tenacious and hard amorphous metal.

If the micrograins of metals result from the granulation of larger primary or macro-dendritic grains, as discussed later, it may be expected that a slower cooling through the granulation zone, that is below solidification, will result in larger micrograins. In other words a slow solidification should result in large dendrites and large macrograins, while slow cooling below solidification should make for large micrograins. Whether *for the same rate of cooling* through the granulation zone larger macrograins will result in larger micrograins has never been shown to the author's knowledge.

The common belief is that prolonged exposure of pure metals to a high temperature (annealing) tends to enlarge the micrograins, the enlargement being the greater the higher the temperature, the longer the time of exposure, and the slower the cooling. It is highly improbable, however, that grain growth will take place unless the metal has been previously strained, as explained in the following pages, or unless, indeed, it undergoes, as iron does, an allotropic transformation at a certain critical temperature.

[1] Private communication to the author.

Carpenter writes: "In the absence of a change of phase, neither crystal growth nor recrystallization will take place in a metal unless it has been plastically deformed and subsequently heated to a certain minimum temperature and for a certain minimum time."

Grain Growth. — It has been seen that when metals are subjected to cold working, the crystalline grains of which they are composed are distorted, that is, elongated in the direction of the work. When such deformed metals are heated (annealed) a crystalline readjustment or recrystallization takes place, tending to remove the distortion due to cold working, that is, to produce equi-axed grains. This crystalline transformation is frequently called "grain growth." The dimensions of the equi-axed grains will be affected by the following factors: (1) Nature of metal, (2) amount of cold work deformation, (3) size of distorted grains, (4) temperature at which deformation was produced, (5) annealing temperature, (6) time at annealing temperature, and (7) rate of cooling from annealing temperature. The grain growth of metals may be explained by the amorphous theory which postulates the existence of an amorphous as well as of a crystalline phase, the former, as previously explained, existing in the cast metal as membranes cementing together the crystalline grains.

In the following description and discussion of grain growth in metals, the author's early work as well as the views of Jeffries and of Howe, so ably presented, are given special consideration.

Assuming the coexistence of two phases, crystalline and amorphous, in any pure metal, it is essential to bear in mind that some of their physical properties differ materially.

According to Jeffries, the cohesion of the amorphous phase is nil at the melting point, while that of the crystalline phase is considerable. On cooling, moreover, the cohesion of the amorphous phase increases more rapidly than that of the crystalline phase, resulting in the equal cohesion of both phases at a certain temperature called by him the "equi-cohesive" temperature. This may be illustrated diagrammatically, as shown in Figure 19, in which the triangle EAF represents the increasing cohesion of the amorphous material with falling temperature, being zero at the melting point, CD at the equi-cohesive temperature, and EF at absolute zero, while the increasing cohesion of the crystalline phase, represented by EABG, is AB at the melting point, CD at the equi-cohesive temperature, and EG < EF at absolute zero.

Since resistance to deformation must be greater the greater the cohesion, it follows that the crystalline phase will cause greater resistance to deformation *above* the equi-cohesive temperature than an equal amount of the amorphous phase, while, on the contrary, the amorphous phase will cause greater resistance to deformation *below* the equi-cohesive temperature than the same amount of the crystalline phase. It follows, in turn, from this consideration that for the same metal a coarse-grained structure, since it contains less amorphous material, will offer greater resistance to deformation *above* the equi-cohesive temperature than a fine-grained structure, while, on the contrary, *below* the cohesive temperature the fine-grained structure will be more resistant to deformation. At the equi-cohesive temperature the resistance to deformation should be the same both for the coarse-grained and fine-grained metals, since the two phases have now the same cohesion. According to Jeffries the rate of loading has a much greater effect on amorphous metal than on crystalline metal, hence rapid loading raises the apparent equi-cohesive temperature.

It is believed that the recrystallization implying grain growth will not take place

until a temperature is reached at which the amorphous phase is less cohesive than the crystalline, from which it would follow that the equi-cohesive temperature must correspond to the *minimum temperature at which grain growth can begin.*

Howe calls "germinative" temperature the temperature at which growth begins, "inert range" the range below the germinative temperature, and "growth range"

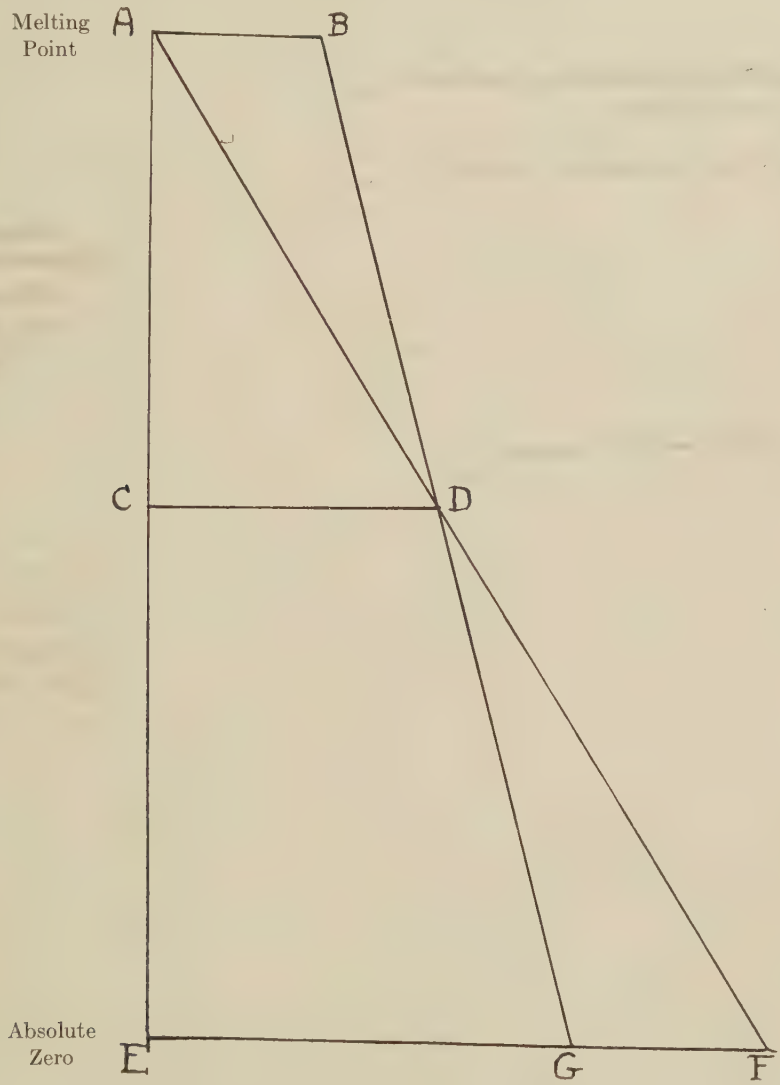


Fig. 19. — Relative cohesions of crystalline and amorphous phases.

that above it. A "germinant" grain is one that is at its germinative temperature and therefore beginning to grow. Germinative temperature has also been called "critical temperature for grain growth" and "equi-axing temperature." It is believed by some that to each temperature corresponds a certain grain size which cannot be exceeded, known as the "equilibrium grain." According to Jeffries, however, "strictly speaking there is no equilibrium grain size until all of a given piece of metal consists of a single grain."

The more severe the deformation the lower the germinative temperature, but the growth is greater at a high germinative temperature, that is, in but slightly deformed metals. This is shown graphically in Figure 20, where the germinative temperature is seen to fall as the deformation increases, while the size of the grain decreases with the falling germinative temperature. For a deformation D, for instance, and germinative temperature T the size of the grain would be represented by AB, while for a deformation $D' < D$ and germinative temperature $T' > T$ the size of the grain is represented by $A'B' > AB$.

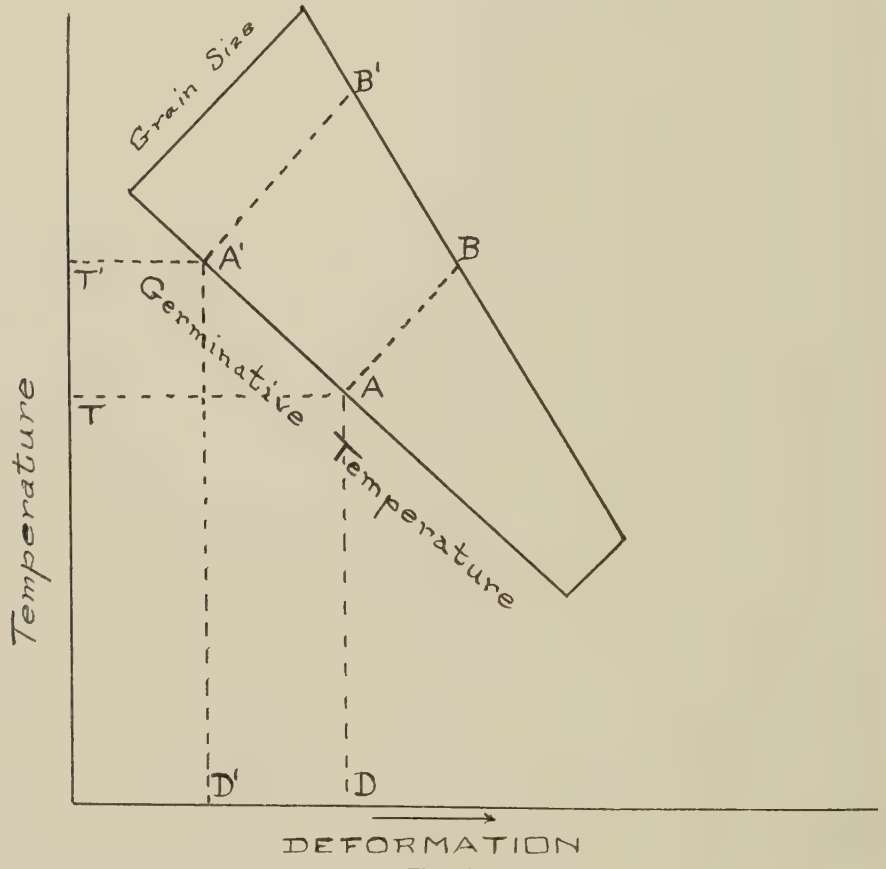


Fig. 20.

The influence of (1) temperature gradient and (2) deformation gradient on grain growth should be mentioned. A temperature gradient is obtained when a portion of a piece of metal is heated to a given temperature, while the portions away from the heated part are necessarily at lower temperature, as for instance in heating a bar of metal at one end; a deformation gradient results from deforming a piece of metal more severely at a given spot than in the surrounding region, as for instance in the Brinell ball hardness test.

The formation of large grains at the germinative temperature appears to be favored both by temperature gradient and by deformation gradient.

Amorphous Cement Theory vs. the Heat Treatment of Pure Metals. — It is believed by Rosenhain and Ewen that the amorphous films cementing together the

crystalline grains of pure metals act as a vehicle for crystal growth under suitable temperature conditions. This intercrystalline amorphous cement might play the part ascribed to eutectic films in Ewing and Rosenhain's earlier theory. While according to the former theory the grains of strictly pure metals could not grow on annealing, even after straining, owing to the absence of eutectic films, the amorphous cement theory permits such growth, and this is in better harmony with observed facts.

The annealing of cold worked metal should result in the transformation of some of the strong but hard and brittle cement resulting from the cold working, as previously explained, into crystallized metal, and this should be accompanied by decreased hardness and increased ductility, thus accounting for the well-known influence of annealing on cold worked metal.

Impurities. — It is well known that the addition of surprisingly small amounts of impurities or foreign substances often affects very greatly some of the most important properties of metals, such as their strength, ductility, fusibility, electrical conductivity, etc., and we naturally look for correspondingly marked changes of structure. This important question is considered at some length in the following chapter.

Addendum. — In a private communication to the author, Professor H. M. Boylston remarks that if both crystalline and amorphous phases do exist together in a pure metal, the latter, according to the phase rule, is out of equilibrium since a one component system cannot contain more than one phase. Boylston's pertinent observation leads us to conclude that all pure metals as we know them are out of equilibrium and in that case any treatment such as prolonged heating at a high temperature which makes for equilibrium should result in the disappearance of one phase, undoubtedly the amorphous one, and to the final formation of a *single* crystal. Only then will the metal satisfy the demands of the phase rule.

CHAPTER II

IMPURE METALS

Impure metals may be logically considered as alloys in which, with the exception of the metal proper, the alloying elements are present in very small proportions. When it is desired to obtain pure iron, for instance, any carbon that may be present is regarded and treated as an impurity; but when steel is wanted, carbon is introduced and an iron-carbon alloy produced. Similarly zinc in what should be pure bronze is an impurity, but zinc is frequently added as an alloying element to copper-tin alloys. It is to be expected that these elements, whether they be present unavoidably as impurities or intentionally introduced as alloying elements, will assume the same forms and exhibit similar behavior.

The study of the occurrence and behavior of impurities in metals must necessarily, therefore, include considerations that pertain as well to the study of alloys. It seems advisable, however, to devote a separate chapter to a general description of the forms assumed by impurities and of the resulting structures.

As mentioned in the preceding chapter, absolutely pure metals can be produced only, if at all, with the greatest difficulty, especially if it implies, as it should, complete freedom from gases. The marked influence, on the other hand, of extremely small quantities of certain impurities on some of the physical properties of metals has been repeatedly demonstrated.

Impurities in metals may be other metals, metalloids, or gases. They may (I) remain uncombined, or (II) they may form a chemical combination (*a*) with some of the metal itself or (*b*) with another impurity. Using the symbols M to represent the metal, and I, I′, I″ the impurities, the forms the latter may assume may be represented by the notations I, I′, I″, M_xI_y or $I_xI'_y$. The possibility of chemical compounds such as M_xI_y and $I_xI'_y$ dissolving in each other, forming double compounds or mechanical mixtures, will not be considered at present. The uncombined impurities (I, I′, I″) and the two types of chemical compounds (M_xI_y and $I_xI'_y$) may (I) be soluble in the solidified metal, giving rise to the formation of solid solutions, or (II) be insoluble in the solidified metal, in which case they will be present (*a*) as inclusions or (*b*) as one of the components of a eutectic or eutectoid alloy. This classification is tabulated below: —

		Resulting micro-constituents
I. Impurities remaining uncombined (I, I′, I″)		I. Soluble in solidified metal — Solid solution
II. Impurities forming chemical compounds	(*a*) With the metal itself. (M_xI_y, $M_xI'_y$)	
	(*b*) With another impurity ($I_xI'_y$)	II. Insoluble in solidified metal — (*a*) Inclusions; (*b*) Eutectic alloy

Obviously nine different forms of these impurities may result from this classification as follows: —

(1) Uncombined impurities in solid solution.
(2) Uncombined impurities as inclusions.
(3) Uncombined impurities as components of eutectic alloys.
(4) Chemical compound of the impurities with the metal as solid solutions.
(5) Same as inclusions.
(6) Same as components of eutectic alloys or of eutectoids.
(7) Chemical compound of two impurities as solid solutions in the metal.
(8) Same as inclusions.
(9) Same as components of eutectic alloys.

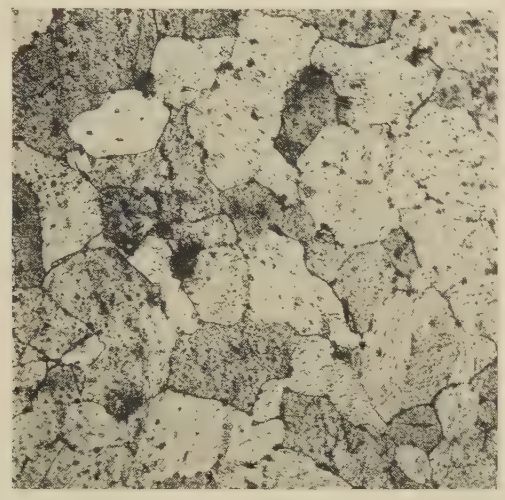


Fig. 21. — One per cent silver in copper, annealed. Magnified 100 diameters (L. R. van Wert.)

Three *types* of structures are consequently to be observed in impure metals corresponding respectively to (1) solid solutions, Fig. 21; (2) presence of inclusions, Figs. 22, 23, 24; and (3) presence of eutectic or of eutectoid alloys, Fig. 25. They should be briefly considered.

SOLID SOLUTIONS

As Professor Howe has well expressed it, the essential features of an ordinary liquid solution are (1) a complete merging of the constituents and (2) in indefinite proportions. By complete merging is meant a union so intimate that the separate existence of the constituents cannot be detected by any physical means, such for instance as microscopic examination under the highest magnification. The homogeneity of the substance is such that it resists any physical attempt at breaking it. The merging, moreover, must remain complete and absolute for varying proportions of the constituents, for it is evident that if it existed only for certain well-defined proportions of the component parts, the resulting substance would be of the nature of a definite chemical compound and not of a solution.

Bearing in mind these characteristics of ordinary solutions, we find that in some substances, in passing from the liquid to the solid state, the constituents remain

completely merged and in indefinite proportions. *The essential characteristics of liquid solutions are retained in the solid state.* Hence the name of solid solutions given to such substances. A common and excellent example of solid solutions is found in the case of glass, in which the three usual constituents, silica, lime, and alkali, are so completely merged that their existence cannot be detected by physical means; the microscopical examination of glass under the highest magnification fails to reveal the presence of its component parts. Glass on solidifying passes from the condition of a liquid solution to that of a solid solution. Many metals likewise form on solidifying solid solutions, i.e. they solidify into a mass so absolutely homogeneous that the identity of the component metals is entirely lost. The union between some metals and metalloids, as well as between metals and some definite compounds, also frequently forms solid solutions.

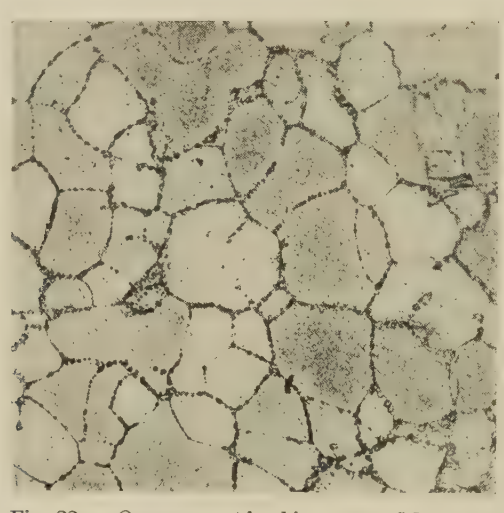


Fig. 22. — One per cent lead in copper. Magnified 100 diameters. (L. R. van Wert.)

It is held by some crystallographers that in order to form solid solutions the uniting substances must be "isomorphous," that is, must be capable of yielding crystals of the same form, hence the name of "isomorphous mixtures" frequently given to solid solutions.[1] The homogeneous crystals formed by solid solutions are often called "mixed crystals" — and that expression is *sometimes* used as an equivalent for solid solution. There are some crystallographers, however, who believe that isomorphism of the constituents is not essential to the formation between them of solid solutions, and that the use, therefore, of isomorphous mixtures as synonymous of solid solution is not warranted. The expression "mixed crystals" is likewise to be discouraged because it suggests a mixture, and therefore, heterogeneity, which is precisely contrary to the nature of solid solutions.

Granular Structure of Solid Solutions. — It will be noticed that the structure of solid solutions (Fig. 21), as revealed by ordinary etching methods, resembles that of

[1] If isomorphism favors the formation of solid solutions, as it undoubtedly does, seeing that most metals are isomorphous, we naturally infer that they will readily form solid solutions. We now know that such is the case, for if metals are not generally soluble in each other (when solid) in *all proportions* there are few instances of metals entirely insoluble in each other in the solid state. The formation of solid solutions between metals is therefore very frequent.

pure metals (Figs. 6 and 7), both consisting of polyhedral crystalline grains. Impurities forming solid solutions with the metal do not alter the character of its structure, although it may affect the dimension of the grains.

Dendritic Structure of Solid Solutions. — By applying to solid solutions the special reagents used to bring out the dendritic structure resulting from dendritic segregation, it is often possible, as shown in Fig. 26, to reveal clearly the presence of dendrites, whereas, as previously explained, the same reagents fail to disclose the dendrites of pure metals. Indeed, the test may be used for the purpose of ascertaining whether a metal exhibiting a polyhedral structure is pure or contains some impurity in the form of a solid solution. The mechanism of the formation of solid solutions on solidification will be considered at some length in another chapter. To account for the readiness with which the dendrites of solid solutions can be disclosed by suitable etching reagents it will suffice for our present purpose to consider a solid solution of a metal M and impurity I and to assume that I has a lower melting point than M. When the liquid solution of these two components begins to solidify, dendritic crystals begin to form at many different centers of crystallization, or nuclei. Let us follow the growth of one such dendrite. The portions of the dendrite forming first, namely the main axis, and then the secondary axes, will contain a relatively small proportion of the more fusible component I. As solidification proceeds, however, *with fall of temperature*, the crystalline matter continuously added in the process of building up the crystallite contains an increasing proportion of I. It is as if the bricks used in building a structure were of different composition, each brick added containing more I than the preceding one. It must necessarily be so, because during the process of solidification of a solid solution the temperature is constantly falling, and to each temperature corresponds a certain proportion of the two components. Only the crystalline elements formed at the same temperature can have identical composition. Many masons are building this structure and they work in perfect harmony, laying bricks of identical composition at exactly the same time, that is at the same temperature and in flawless symmetry. Chemical heterogeneity, therefore, exists in the completed dendrites, the portions having formed first, that is at the highest temperature, containing less of the low-melting-point constituent than the portions formed later at a lower temperature. It follows that the metal filling up the interstices between the axes or branches, and which necessarily was late in solidifying, will contain a greater proportion of I, and likewise that the amorphous cement assumed to exist at the boundaries of adjacent dendritic growths will contain still more of I since it was the last to solidify. This chemical heterogeneity is frequently described as due to the segregation of the impurity I in portions solidifying late or last. It is this chemical heterogeneity, as previously mentioned, that makes possible the disclosure of the existence of dendrites through the selective action of suitable reagents. Certain reagents holding copper salts in solution, for instance, will frequently cause the deposition of metallic copper on the purest parts of the dendritic structure, that is on the axes, while leaving the more impure portion or fillings unaffected, or but slightly coated, thereby revealing the hidden structure. In the majority of cases, however, the heterogeneity existing in each dendrite, immediately after its formation, is not retained unimpaired at room temperature. The phenomenon of diffusion sets in immediately a dendrite forms, the tendency of which is to bring about the chemical homogeneity demanded by the law of equilibrium. To explain the mechanism of this diffusion, we must assume that some of the molecules rich in I present in certain

portions of the dendritic structure migrate into the portions poorer in *I* to be replaced by molecules containing little *I*, and vice versa. Should this diffusion become complete it is obvious that at room temperature each dendrite would be so perfectly homogeneous that it would no longer be possible to reveal its existence through the selective action of suitable reagents. This is precisely why, as already pointed out, the dendrites of pure metals cannot be disclosed by these reagents.

The two conditions so far considered, (1) complete absence of diffusion, the dendrite retaining at room temperature the chemical heterogeneity it possessed immediately after its formation, and (2) diffusion completely effacing such heterogeneity, are extreme cases. In the greater number of instances diffusion will take place but will remain incomplete, the dendrites at room temperature retaining sufficient heterogeneity to permit their disclosure by etching methods. This will be referred to in these pages as persistent dendritic segregation.

As might be anticipated, very slow cooling and long sojourn at high temperature will promote diffusion and homogeneity, while quick cooling immediately after solidification will tend to preserve the heterogeneity of the dendrites. The power of diffusion of the segregated elements varies greatly, some diffusing very readily, others with much difficulty. The readiness and clearness with which the dendritic structure of solid solutions can be revealed by etching may be taken, therefore, as an indication of the degree of heterogeneity of the crystallites. Again, of two impurities dissolved in a metal one may diffuse readily, while the other may remain segregated. In iron containing both carbon and phosphorus, for instance, it is generally believed that carbon diffuses with ease while phosphorus does not, and that the selective action of certain copper reagents by which the existence of dendrites is revealed is due to this persistent phosphorus segregation. It should be remembered also that gases as well as solid elements may cause dendritic heterogeneity. Oxygen, for instance, may combine with some of the metal and the resulting oxide may produce dendritic segregation. Le Chatelier believes that oxygen present as FeO rather than phosphorus is responsible for the possibility of bringing out the dendritic structure of iron and steel. The formation of dendrites in iron and steel will be further considered in another chapter. The dendrites of solid solutions are frequently so large that they can be readily seen with the naked eye. They are then said to be macroscopic. Obviously, however, macrostructures and dendritic structures are not synonymous. Dendritic structures are not necessarily macroscopic and macrostructures not necessarily composed of dendrites. The important question of the dendritic crystallization of solid solutions is discussed at greater length in Chapter X, where solid solutions of iron and carbon are considered.

Impurities forming solid solutions with the contaminated metal increase its hardness and tenacity while decreasing its plasticity and malleability and generally its ductility; its electrical conductivity is also usually diminished. They raise or lower the melting point in accordance with their own fusibility. They decrease the weldability of weldable metals.

Crystal Structure of Solid Solutions. — It is believed by many that in most solid solutions the atoms of the solute (*I* in the present instance) replace some of the atoms of the solvent without changing the character of its space lattice. If the latter has a face-centered cubic lattice, for example, the same type of lattice will still be found to exist in the solid solution. According to Rosenhain, the presence of foreign atoms in the lattice of the solvent distorts it, and this distortion, by offering greater resist-

ance to slip, explains the greater hardness of solid solutions. Jeffries and Archer, however, attribute this increase of hardness partly to a greater attraction between unlike atoms and partly to a roughening of slip planes due to the difference in size between solvent and solute atoms.

There are some who believe that chemical compounds cannot exist as such in solid solution. We are told that their solution implies dissociation and their precipitation from solid solution involves, as a matter of fact, their *formation*. They base their contention on the ground that there is no room for molecules in the cubic lattices of crystals.

Inclusions. — Impurities in metals may be retained as such in the form of small particles embedded in the metals (Fig. 22), or they may combine with some of the

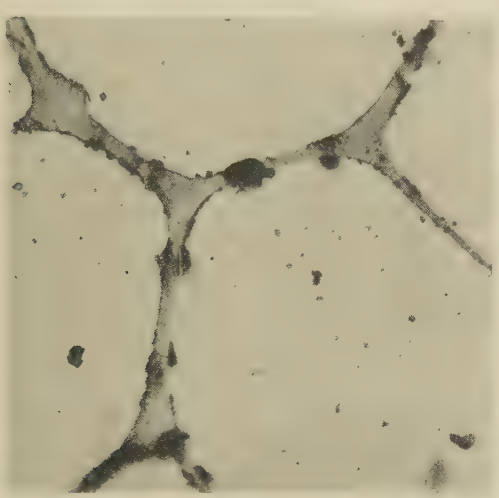


Fig. 23. — FeS in iron. (V. N. Krivobok, in the author's laboratory.)

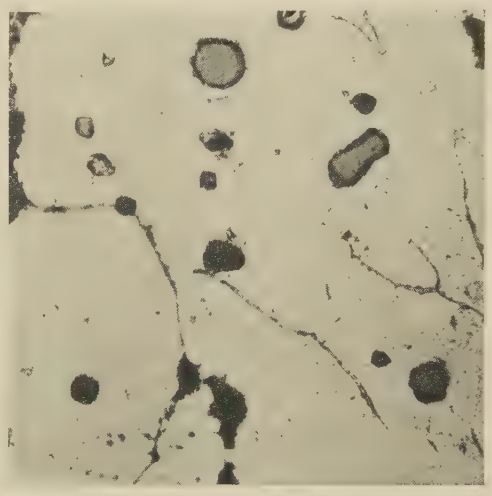


Fig. 24. — MnS in iron. (V. N. Krivobok, in the author's laboratory.)

metal or with another impurity and the resulting compounds embedded in the metal (Figs. 23 and 24). Impurities existing in this form are known as "inclusions" or "enclosures." Their presence is generally revealed by the polishing operation without the assistance of any etching reagent. The influence of inclusions on some of the physical properties of the metal they contaminate must necessarily depend upon (1) their nature, (2) their amount, (3) the size of the particles, (4) the form of the particles, and (5) their distribution. Their action is generally due more to the fact that they break up the continuity of the metallic mass rather than to their own physical properties. The presence of some inclusions of a ductile substance, for instance, may be more effective in decreasing the ductility of a metal than the presence of particles of a more brittle nature if the continuity of the metallic mass is more thoroughly broken up by the former. This would be the case if the ductile inclusions occurred as sharp plates or sheets. Inclusions segregated in certain parts of a metallic mass will obviously cause local weakness and intensive alteration of some of the physical properties of the segregated portions. Inclusions that are plastic at the temperature the metal is worked are elongated in the direction of the work, as for instance manganese sulphide (MnS) in iron, and may then impart a fibrous appearance to the metal, as in the case of slag in wrought iron.

When inclusions have a tendency to form more or less continuous membranes around the grains, their influence becomes more pronounced, and if in addition they have a lower melting point than the metal, they may be a cause of red-shortness, their early melting causing a weakening of the cohesion between the grains: witness the red-shortness of steel resulting from membranes of iron sulphides (FeS) partially surrounding the grains.

Eutectic Alloys. — The constitution and formation of eutectic alloys will be found fully described in Chapter XXIV. For our present purpose it will suffice to explain that when a metal *M* containing an impurity *I*, forming with it a eutectic alloy, solidifies, pure crystals of the metal *M* are first formed, increasing in proportion *as the temperature falls* until finally the portion remaining liquid contains the impurity in

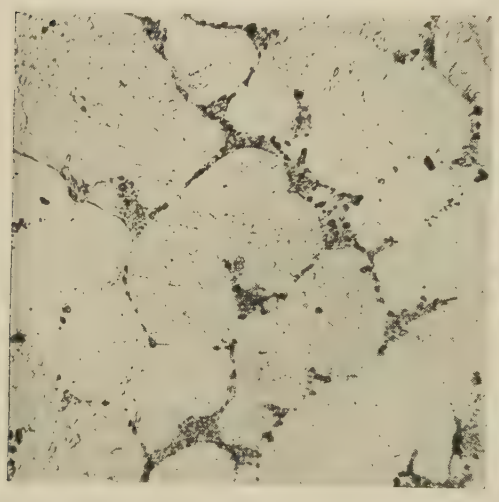


Fig. 25. — Eutectic of $Cu-Cu_2O$ in copper. Magnified 100 diameters. (L. R. van Wert.)

Fig. 26. — One per cent silver in copper. Magnified 100 diameters. (L. R. van Wert.)

so-called eutectic ratio. This last portion now solidifies at a *constant temperature* through the formation of very small crystals alternately of the metal *M* and the impurity *I*, frequently in the form of parallel plates (Fig. 25). The components constituting this eutectic mixture are always associated in constant, but *not in atomic*, proportions. The solidified metal finally consists of small particles of eutectic embedded in the metal. The influence of a small amount of eutectic particles is not unlike that of inclusions: by breaking up the continuity of the metallic mass they generally decrease its strength and ductility. If present in sufficient quantity to surround partially the grains, they may affect more seriously some of the properties of the metal and may be a cause of red-shortness because of the possibility of their melting at the temperature at which the metal is worked, thereby diminishing the cohesions between adjacent grains.

Impurities as Crystallizing Nuclei. — Some writers believe that in slightly impure metals the impurities may form nuclei from which crystal growth may start, thus accounting for the apparent fact that slightly impure metals have often smaller grains than metals of greater purity. This assumption demands an early solidification of small particles of impurities within the liquid metal, and therefore can be

true only in the case of foreign substances having a higher melting point than the metal itself. It is not easily conceived how it can be applied to impurities forming solid solutions with the metal, since they then solidify together, nor to impurities forming eutectic alloys, since such alloys constitute the constituent of last solidification. Only those impurities which are known as inclusions, it would seem, can act as crystallizing nuclei, and then only when they solidify before the metal.

CHAPTER III

PURE AND IMPURE IRON

Frequent attempts have been made to obtain chemically pure iron, but while it has been found possible to prevent almost completely contamination by the usual impurities, carbon, silicon, sulphur, phosphorus, and manganese, complete elimination of gases is quite impossible. When the metal is obtained by fusion with free access of air, it absorbs oxygen, nitrogen, and hydrogen, and subsequent remelting in vacuum fails to expel completely those gases, while if the iron is produced electro-

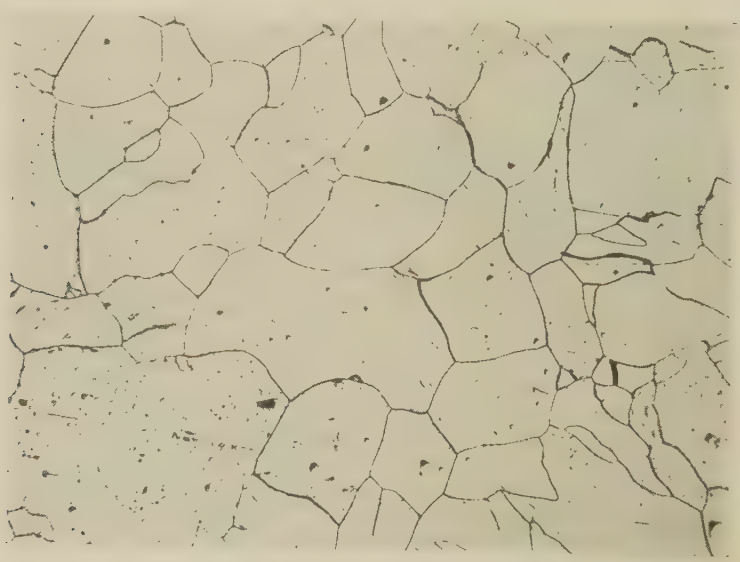


Fig. 27. — Electrolytic iron, annealed. 125 diameters. (D. C. Lee, in the author's laboratory.)

lytically it contains hydrogen, likewise impossible of complete elimination by vacuum melting.

Electrolytic iron is now commercially obtainable of a degree of purity frequently exceeding 99.95 per cent iron. It is manufactured at Grenoble, France, by the Société Le Fer and at Niagara Falls by the Niagara Electrolytic Iron Company.

The American product of the open-hearth furnace, known as "American ingot iron" or "Armco," universally known and so widely used, generally contains more than 99.90 per cent of iron.

It would be unwise, however, to assume that the few hundredths of one per cent of impurities remaining in these very pure products can have no appreciable influence on the physical properties of the metal.

Granular or Polyhedral Structure of Iron. — When a sample of nearly pure iron is suitably prepared and examined under the microscope it is found to be composed, like other pure metals, of allotriomorphic crystals in the form of crystalline grains. Such structure is illustrated in Figures 27 and 28 after a slight etching of the polished surface. Upon deeper etching the dissimilarity, as to coloration, of adjacent iron grains is clearly brought out as shown in Figure 29. It has been explained in Chapter I that this appearance is due to the fact that the grains of iron are composed of crystalline elements having the same orientation in the same grain but different ones in different grains.

As previously stated, it is believed by some that the crystalline grains of iron like those of other pure metals are surrounded by thin membranes of amorphous cement (the network in Figs. 27 and 28) holding the grains together, this amorphous metal being harder and stronger but less ductile than the crystalline grains themselves. Before this theory had been advanced it was generally assumed that the grains were

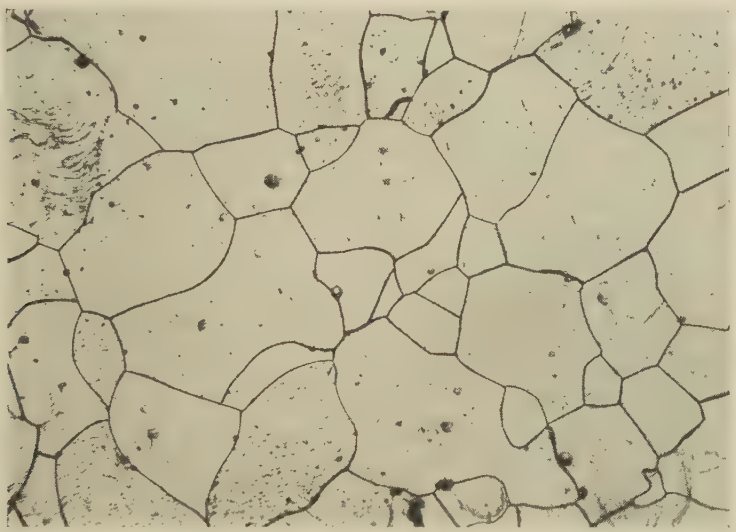


Fig. 28. — American ingot iron, annealed. Magnified 125 diameters. (D. C. Lee, in the author's laboratory.)

held together by surface contact alone or cohesion and that the network revealed on etching merely indicated sections through these contact surfaces made apparent owing to slight differences of solubility of adjacent grains (because of their different orientation) and resulting in slight differences of level after etching.

Cubic Crystallization of Iron. — A still deeper etching indicates clearly the cubic character of the crystallization of pure iron. This is illustrated diagrammatically in Figure 30 and by means of a photomicrograph in Figure 31. It will be noted that the etching pits are similarly oriented in the same grain but that the orientation in adjacent grains differs. This cubic structure is further illustrated in a remarkable manner in Figure 32, in the case of iron containing 4½ per cent of silicon after etch-

ing three hours in dilute nitric acid. The photograph shows a portion of a single grain, hence the constancy of orientation noted. The presence of so much silicon apparently favors the development of a coarse cubic crystallization.

Osmond, through the reduction of ferrous chloride and the crystallization of the resulting metallic iron, obtained perfect isolated cubic crystals (Fig. 33).

Fig. 29. — Ferrite grains. Natural size. Etched 10 minutes in nitric acid (1 to 10 water). (Stead.)

Fig. 30. — Etching pits in iron. (Desch.)

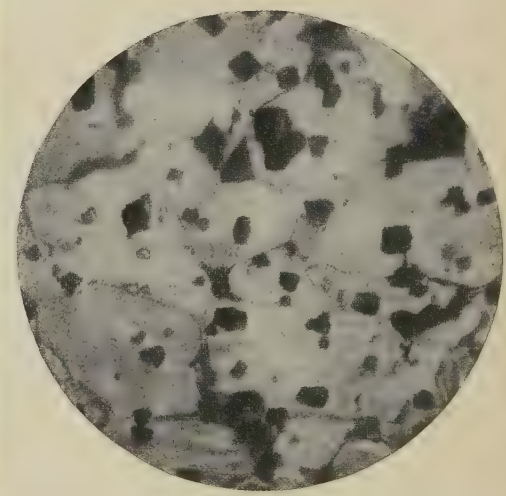


Fig. 31. — Etching pits in ferrite. (J. F. Hoyland, Correspondence Course student.)

The octahedral character of the dendrites formed on solidification is another evidence of cubic crystallization. Finally, X-ray analysis has shown that alpha iron had a body-centered, and gamma iron, a face-centered cubic lattice.

Dendritic Structure of Pure Iron. — There is little doubt but that the solidification of pure iron like that of other pure metals results in the formation of dendrites. If the etching methods used to bring out the dendritic structure of metals and alloys fail to reveal the presence of dendrites in pure iron, it is because, as previously ex-

plained, each dendrite necessarily possesses complete chemical and physical homogeneity, whereas heterogeneity is essential for the selective action of the etching reagent. It should be remembered, however, that a very small amount of a certain impurity may be sufficient to produce the needed dendritic heterogeneity. The tendency of phosphorus, for instance, to segregate during solidification and its resistance to diffusion is believed to be sufficient to produce the needed heterogeneity even when but a trace of that element is present. Nor should it be forgotten that gases as well as solids may produce heterogeneous dendrites. It is possible that the discovery of etching reagents more delicate and searching in their action than those at

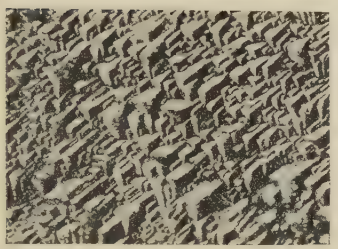


Fig. 32. — Silicon steel, 4.5 per cent silicon. Magnified 60 diameters. Part of a single grain. Etched 3 hours in nitric acid (1 to 10 water). (Stead.)

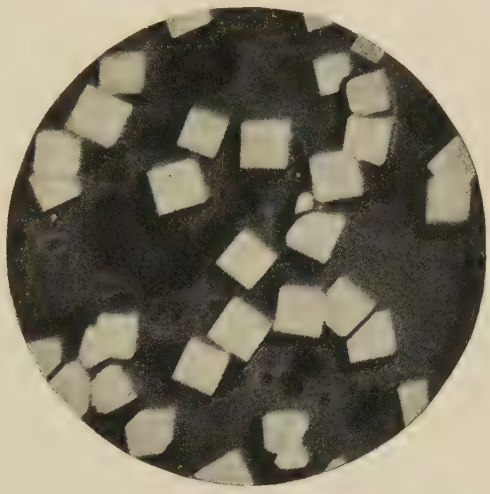


Fig. 33. — Cubic crystals of iron. Magnified 250 diameters. Obtained through the reduction of ferrous chloride. (Osmond.)

present available might result in the detection of dendritic structures which now remain hidden. The dendrites of pure and of impure iron and the resulting grains are generally of macro-size, that is, of such large dimensions that they can be observed with the naked eye. Belaiew believes, however, and his contention is well supported, that as the iron cools below solidification to the critical range, *granulation* of the dendrites takes place, resulting in the formation of the small micrograins observed under the microscope. In other words, the solidification of pure iron results in the formation of dendrites of macro dimensions, giving rise to large grains which we may call the primary grains, while its subsequent cooling below solidification results in the breaking up of those large grains into small microscopic grains which we may call secondary grains and which constitute the structure observed under the microscope.

It will later be explained that in cooling, iron undergoes at about 900° C. an allotropic transformation, passing from the gamma to the alpha (or beta) condition, and involving the transformation of each small grain of gamma iron into a grain of alpha (or beta) iron. These views have been summed up diagrammatically in the following table. The dendritic structure of iron and of its alloys and the probable granulation of dendrites will be considered at greater length in the further treatment of our subject.

1530°C. — Solidification of pure iron. Formation of dendrites and of large macrograins of gamma iron.[1]

Granulation zone.

Breaking up of dendrites into small (micro-) grains of gamma iron.

900° C. — Allotropic transformation of micrograins of gamma iron into micrograins of alpha iron. (Final microstructure.)

Ferrite. — Mineralogical names have been given to the constituents of iron and steel; pure iron, or rather carbonless iron, considered as a microscopical constituent has been called "ferrite," a name suggested by Prof. H. M. Howe and universally adopted.[2] Pure iron, therefore, is composed of polyhedral crystalline grains of ferrite, each grain resulting probably from the breaking up of larger grains of gamma iron, which in turn are the products of dendritic growth. It will be seen in subsequent chapters that the ferrite of commercial grades of iron and steel is not pure iron, but rather iron holding in solid solution small amounts of silicon, phosphorus, and possibly other impurities. Stead has suggested that when ferrite consists only of pure iron it should be called "ferro-ferrite."

Allotropy of Iron. — The study of the crystallization of iron is complicated by the existence of several allotropic forms of that metal.

Physicists and chemists do not agree as to the exact meaning of allotropy, still less as to the phraseology by which it should be defined. Allotropy certainly implies marked and sudden reversible changes taking place in some of the properties of a substance at certain critical temperatures excluding formation or dissociation of chemical compounds and changes of state although the latter might be considered as major instances of allotropy. Opinions differ, however, as to whether a well-defined change in a single property constitutes a proof of allotropy, while some scientists insist that unless a crystallographic change is observed at the critical temperature the transformation cannot be considered an allotropic one.[3] Again it is claimed by some and denied by others that a spontaneous evolution of heat on cooling at a certain critical temperature and absorption of heat on heating at the same or nearly the same temperature, when not accompanied by changes of state or formation or dissociation of chemical compounds, is sufficient proof of an allotropic change. Others still consider the occurrence of a sudden dilatation on cooling and contraction on heating as the best criterion of the existence of allotropy. Finally, in discussing the allotropy of iron it has been attempted by some writers, arbitrarily it would seem, to exclude magnetic changes from those indicative of allotropy.

Many substances undergo allotropic changes. It is a matter of common knowledge, for instance, that sulphur exists under two distinct conditions, namely, as prismatic sulphur and as octahedral sulphur, the prismatic form being the one stable above 95.6 deg. C. and the octahedral, the stable form below that critical tempera-

[1] Some believe that iron solidifies as delta iron, transforming into gamma iron at about 1400°C.

[2] This constituent was called "free iron" by Sorby, who was the first scientist to describe the microscopical structure of iron and steel.

[3] The property of some substances of crystallizing in more than one form is called polymorphism. The expression, however, should not be used as an equivalent of allotropy.

ture. On heating octahedral sulphur it begins to change into the prismatic form at the temperature of 95.6 deg. and, likewise, on cooling, prismatic sulphur begins to pass to the octahedral form at that temperature. Many of the physical properties of sulphur (crystalline form, specific heat, heat of combustion, etc.) undergo sudden changes as the substance passes from one allotropic form to another.

At those critical temperatures which mark the passage of one allotropic form into another, spontaneous evolutions of heat take place on cooling and spontaneous absorptions of heat on heating. These thermal disturbances indicate a change of internal energy which when not accompanied by changes of state or by chemical changes are in the author's opinion evidences of allotropy. The usual method of detecting the existence of such thermal critical points will be described in another chapter.

Osmond's momentous discovery of the existence of two thermal critical points in pure iron respectively at about 768 and 900 deg. C. was at first accepted as proving the occurrence of iron under three allotropic varieties, γ (gamma) iron stable above the upper critical point, β (beta) iron stable between the two points, and α (alpha) iron stable below the lower point. The allotropic character of gamma and alpha iron is still universally accepted, and indeed has been firmly established, but it is contended by some that the condition of iron between its two critical points does not differ allotropically from its condition below its lower critical point; in other words, that the belief in beta iron as a distinct allotropic variety should be abandoned. This important question will be considered at greater length in the chapters of this book dealing with the Thermal Critical Points of Iron and Steel, with the Hardening of Steel and with the Equilibrium Diagram of Iron-Carbon Alloys, when it will be shown that these opposite views result apparently from different conceptions as to the nature of allotropy. For our present purpose it will be assumed that iron exists, as first described by Osmond, under three allotropic conditions.

According to Professor Honda and others, a third thermal critical point occurs at about 1400° C., the condition of the iron above that temperature being designated as delta. Delta iron is claimed to be body-centered like alpha iron. If crystal structure is taken as the criterion of allotropy, it follows then that delta iron is not allotropically different from alpha iron.

As should be expected the passage of one allotropic form into another implies corresponding and, generally, sudden changes in many of the physical properties of iron. Gamma and alpha iron at least differ widely in regard to many of their physical characteristics. It is only desired in this chapter, however, to inquire into the possible differences of crystallization which may exist between the three allotropic conditions of iron, leaving for later consideration the modification of the other properties.

Osmond and, later, Osmond and Cartaud have carefully investigated the difficult problem of the crystallization of the different allotropic forms of iron. Their conclusions were (1) that the three allotropic forms of iron crystallize in the cubic system, (2) that octahedra are the prevailing crystalline forms of gamma iron, (3) that the cube is the prevailing form of beta and of alpha iron, (4) that beta and alpha iron are capable of forming isomorphous mixtures (solid solutions), (5) that gamma iron does not form isomorphous mixtures with beta or alpha iron.

We also have the statement of Osmond that the transformation of gamma iron into beta iron appears to include a change in the planes of symmetry, at least in carburized iron.

Again it has been shown by Osmond and confirmed by other investigators that the occurrence of twinnings is frequent in gamma iron (Fig. 34), while beta and alpha iron are free from them. Neumann bands, on the contrary, may be produced in alpha iron, but not, so far as known, in gamma or beta iron. (See Fig. 18.)

It follows from Osmond's experiments that the allotropy of beta iron could not be proved by its crystallography, since in that respect it does not differ from alpha iron. While, however, in the instances of allotropy which have been noted and

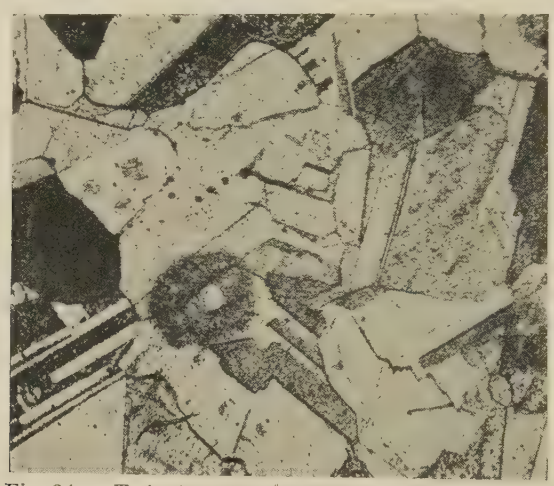


Fig. 34. — Twinnings in gamma iron. Armco iron heated to 980 degrees C. in hydrogen and quenched in water. Magnified 100 diameters. (C. S. Conover and R. P. Thompson, in the author's laboratory.)

studied, allotropic changes are generally accompanied by changes of crystalline forms, it does not by any means follow that any allotropic transformation must necessarily imply a crystalline change unless we arbitrarily demand it.

Assuming the possible existence of four allotropic conditions of iron, — delta, gamma, beta, and alpha, — let us follow in our imagination the crystallization of iron during solidification and its subsequent cooling to room temperature. On solidifying, iron crystallites or dendrities are formed, consisting of octahedral crystals of delta iron with body-centered space lattice. At 1400° C. delta iron is allotropically transformed into gamma iron with face-centered space lattice. Upon further cooling no change of crystalline form should take place unless it be the granulation of the dendrites described by Belaiew and to be considered at greater length later, until a temperature of 900° C. is reached, when gamma iron transforms into beta iron (or according to many, into alpha iron), again assuming a body-centered cubic lattice. Does this transformation affect the size of the grains, or does it consist merely in a transformation *in situ* of each crystalline grain of gamma iron into a grain of beta or of alpha iron, retaining the original external form of the gamma grain, and leaving undisturbed, therefore, the polygonal structure observed under the microscope? It may be reasonably supposed that the allotropic transformation takes place without affecting the external form of the crystalline grains, but in view of Osmond's statement that the octahedron is the prevailing crystalline form of gamma iron and bearing in mind that the small crystals revealed by suitable etching of pure iron are generally

cubic, we naturally infer that the octahedral character of each grain of gamma iron has been obliterated, the small octahedral elements of gamma iron having been replaced by small cubic elements of beta (or of alpha) iron. These conclusions, however, should be accepted with reserve, as we lack evidences of a very conclusive character. It has been shown that the change of gamma iron into beta (or alpha) iron is accompanied by an abrupt expansion of the cooling metal, which expansion is followed by the normal contraction of cooling substances. We infer from this that, momentarily at least, each grain of beta or alpha iron occupies more space than its gamma iron progenitor.

As previously stated, X-ray analysis reveals the fact that gamma iron has a face-centered cubic space lattice which is the atomic configuration corresponding to the closest packed atoms, while both beta and alpha iron have a body-centered cubic space lattice, this being interpreted by those who do not believe in the allotropic character of beta iron as an additional evidence of the correctness of their views.

At 750 deg. C. or thereabout, the iron passes from the beta to the fourth or alpha form, assuming of course that we believe in the allotropic character of this thermal critical point.

We may here ask the same questions as to the probable effect of this change upon (1) the outward form of each beta grain and (2) upon the internal crystalline structure of each grain. Since both beta and alpha iron crystallize in the cubic system, the cube being the prevailing crystalline form of both, and since, according to Osmond, they are isomorphous, that is capable of forming solid solutions, it seems probable that the change of beta to alpha iron affects neither the external form nor the internal crystalline arrangement of the beta grains; in other words that each small cubic element of beta iron is converted bodily (although probably gradually and not abruptly) into a cubic element of alpha iron.

Rosenhain and Humfrey by straining a bar of iron heated to a high temperature at the center (the temperature, therefore, decreasing towards both ends) have made evident the existence of three distinct kinds of distortions with sharp lines of demarcation between them, corresponding in all probability to the distortion respectively of gamma, beta, and alpha iron. The estimation of the temperature of different portions of the bar by means of fusible salts appears to sustain these authors' contention, thus furnishing an additional support, and a substantial one, to Osmond's brilliant theory of the allotropy of iron.

Twinnings and Neumann Bands. — It has been already stated that, according to Osmond and Cartaud, twin crystals frequently occur in gamma iron. It will be shown later, however, that gamma iron, which exists normally only above the upper critical point of iron, requires for its preservation at atmospheric temperature the presence of a considerable amount of carbon, and of other elements, such as manganese and nickel. The twin crystals of gamma iron shown in Fig. 34 do not refer to pure gamma iron but to gamma iron containing a considerable amount of nickel.

Ferrite grains not infrequently exhibit the presence of Neumann bands, which, as previously stated, are mechanical twins, generally resulting from sudden deformation produced by dynamic stresses. Samples that have failed to rupture often contain more Neumann bands than fractured samples because they are generally more severely deformed. In a very sudden rupture the deformations are confined to the close vicinity of the fracture, hence also the Neumann bands. An illustration of Neumann bands in ferrite grains of low carbon steel has been shown in Figure 18.

It has been mentioned in the preceding chapter that in order to distinguish be-

tween slip bands and Neumann bands the specimen should be repolished and again etched, a treatment which should result in the reappearance of the Neumann lines but not generally of slip bands since the latter are merely slight differences of level erased by the polishing operation.

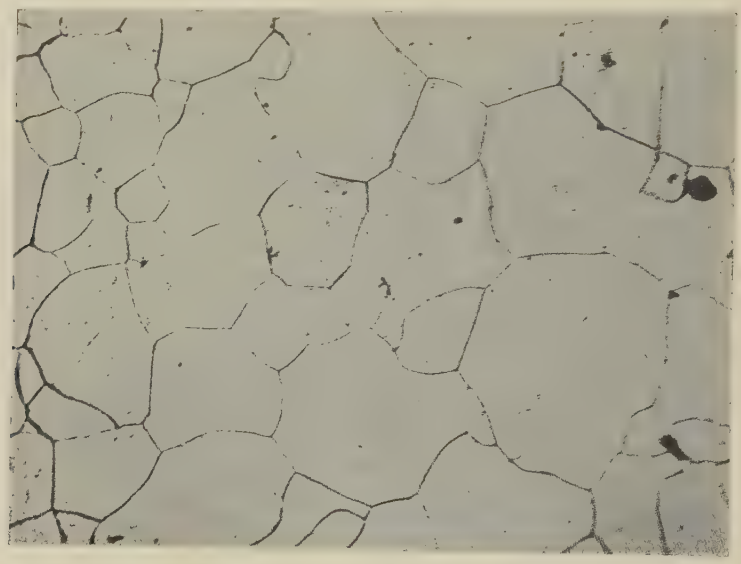


Fig. 35. — Iron before straining. (Rosenhain.)

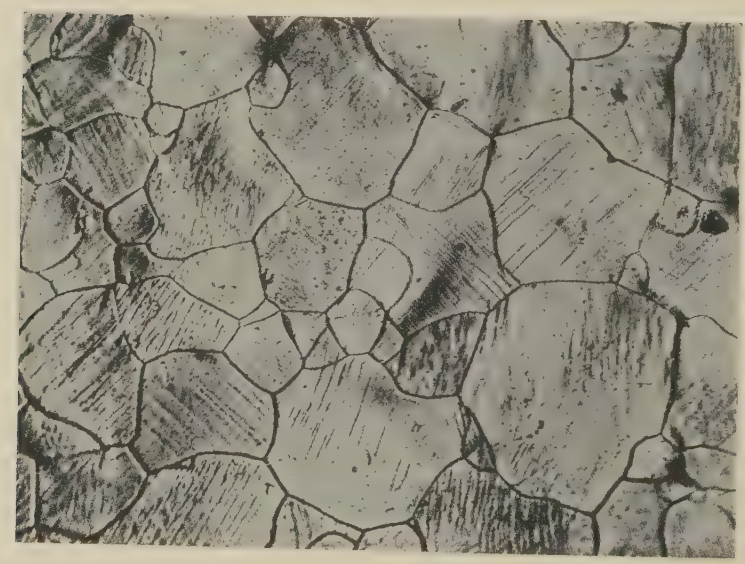


Fig. 36. — Same as Fig. 35 after straining. (Rosenhain.)

Strains and Slip Bands. — It has been shown by Ewing and Rosenhain that like other metals, iron when subjected to a strain exceeding its elastic limit yields through a succession of small crystalline slips readily distinguishable on a polished surface as one or more systems of parallel lines (Figs. 35 and 36). It has been observed by

these authors that this slipping occurs most readily along octahedral planes, from which it would seem to follow, as already noted, that these gliding planes are not identical to cleavage planes since the latter are cubic.

According to Humfrey the slip bands which form first are confined almost entirely to the central parts of the crystals and only spread gradually towards the boundaries as the straining becomes more severe, when they show a tendency to become narrower and to bend so as to meet them at a smaller angle.

As explained in Chapter I it is believed by some that the severe straining of the iron crystals at the gliding planes must result in the formation of thin layers of amorphous metal and that this theory affords a satisfactory explanation of the marked influence of cold working on the physical properties of iron.

The slip bands produced on the polished surfaces of metals by straining are readily visible under the microscope without requiring any further treatment of the sample. This is easily explained on the assumption that they correspond to steps resulting from as many crystalline slips along gliding planes. It is generally stated, however, that upon repolishing and etching after straining, the slip bands disappear, since in so doing we have necessarily eliminated the steps. I believe that this statement can be challenged and that it will be found that slip bands frequently reappear persistently after repeated polishing and etching. Nor is this to be a source of surprise if we assume the formation of amorphous layers along the gliding planes. The polishing operation removes the step-like patterns imparted to the polished surface by straining, but it does not remove the amorphous layers, and the existence of these layers should suffice to indicate the position of the slip bands. In other words, the presence of amorphous cement should reveal the slip band as it does the boundaries of the crystalline grains.

Howe writes: "Whether the slip bands below the surface in ferrite can be detected by cutting, polishing, and etching sections is in dispute; but if this detection is possible at all, it is usually made impossible by heating the metal even gently."

Influence of Mechanical Treatment. — Like that of other metals the structure of iron is affected by mechanical work. Undisturbed cooling being a necessary condition to the free development of crystals, it will be evident that if the metal be vigorously worked, that is subjected to powerful mechanical pressure, while cooling from a high temperature, the formation of crystalline grains will be greatly hindered or preëxisting crystals broken or distorted. The important influence of work upon the structure (and therefore upon the properties) of iron and steel will be duly considered in these pages.

Influence of Thermal Treatment. — The size of the crystalline grains of iron is affected, as is the case with other metals, by the speed of its solidification and subsequent cooling, slow cooling promoting the formation of large grains. When the iron is produced in a pasty condition as in the puddling process and the charcoal hearths, the dimensions of its grains depend essentially upon the temperature from which the metal is allowed to cool undisturbed by mechanical work.

As explained in Chapter I it seems probable that *pure* metals do not undergo any crystalline growth on reheating (annealing) *unless they have been previously strained.* For similar reasons we may doubt the occurrence of any crystalline growth on annealing chemically pure iron *in the complete absence of strain*, assuming that the annealing operation does not result in any allotropic transformation, that is, that it be conducted below 900 deg. C.

The influence of heat treatment upon the structure and physical properties of commercial irons and steels will be dealt with at length in these pages.

Influence of Impurities. — Commercial iron is always contaminated by the presence of at least five elements, namely, manganese, silicon, phosphorus, sulphur, and carbon. The important question of the influence of these substances upon the structure and, therefore, upon the properties of iron and steel will be fully considered in another chapter, when it will be shown that these elements form definite compounds with iron, FeSi, Fe_3C, Fe_3P, or with each other, Mn_3C, MnS, and that some of these compounds, FeSi, Fe_3P, are retained by the iron in solid solution, while others, Fe_3C, Mn_3C, MnS, are rejected to the boundaries of the crystalline grains or along other crystallographic planes, the former two giving rise to the formation of eutectoid mixtures, the latter to inclusions. This behavior of the impurities of iron and steel conforms with the general behavior of impurities described in Chapter II.

CHAPTER IV

WROUGHT IRON

Wrought iron is the name generally given to iron sufficiently free from carbon and other impurities to be malleable when such metal is manufactured through the reduction of iron ores or the refining of cast iron at a temperature so low that it is obtained in a pasty condition and, therefore, mechanically mixed with a considerable amount of the slag formed during the operation. In England wrought iron is also called malleable iron.

When the refining treatment is conducted at a temperature sufficiently high to deliver the resulting products in a molten condition, the refined metal which is then free from slag is called steel.

When containing little carbon this cast metal used to be called "ingot iron." Indeed in Germany the term ingot iron has been applied to the mild steels produced by the Bessemer process. The term has been revived by the American Rolling Mill Company and applied to an extremely pure product of the basic open-hearth furnace which contains less than 0.02 per cent carbon and less than 0.035 per cent manganese. It represents the nearest approach to the element iron commercially obtainable, and it would be incongruous to call it steel. It is also known to the trade and to Science as "Armco" ingot iron.

Wrought iron and steel may otherwise have identical chemical composition, although usually steel contains more manganese and less silicon than wrought iron, often more carbon and less phosphorus.

The author has proposed the following definitions to distinguish between various iron and steel products:

Commercial Iron. — Commercial iron is the element iron as pure as it can be commercially produced.

Ingot Iron. — Ingot iron is commercial iron which has been produced in a fluid condition and cast.

Wrought Iron. — Wrought iron is a ferrous metal which is malleable and which has been produced from a pasty condition.

Steel. — Steel is a malleable alloy of iron and carbon, usually containing substantial quantities of manganese.

As no criticisms of these definitions have ever been received, although repeatedly invited, the author infers that they have generally been accepted as sound and satisfactory.

Wrought iron is sometimes called "puddle" or "puddled" iron, from the name of the furnace in which it is now generally manufactured. Wrought iron made in the old charcoal hearths either directly from the ore or from pig iron (Catalan, Lancashire, or Walloon processes) is called "charcoal hearth" or "charcoal" iron. Wrought iron

produced in the puddling furnace from small pieces of steel scrap is known as "busheled" iron, apparently from the fact that the small pieces of steel used can be gathered in bushel baskets. The product resulting from the reheating to a welding heat and subsequent working of piles (fagots or faggots) of pieces of wrought iron and steel scrap is called "fagoted" iron, also spelled "faggoted" iron. Knobbled iron is wrought iron produced by the knobbling process, which resembles the South Wales process, in which pig iron is first melted down in a coke refinery, considerable silicon and carbon being eliminated, and then treated in a charcoal hearth somewhat as in the Lancashire process.

Puddled iron and charcoal hearth irons are generally freer from manganese than fagoted and busheled irons, while charcoal hearth iron generally contains less phosphorus and less slag than puddled iron.

When wrought iron contained enough carbon to be hardened by quenching it was at one time called wrought steel, but this expression is now obsolete.

Fig. 37. — Wrought iron. Longitudinal section. Magnification not stated. (Longmuir.)

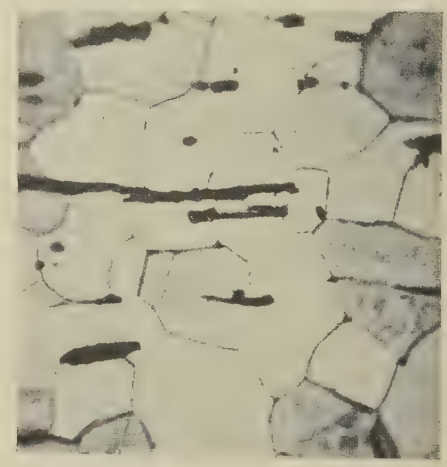


Fig. 38. — Wrought iron. Longitudinal section. Magnified 250 diameters. (R. H. Greaves and Harold Wrighton.)

In the puddling process the pasty lumps of iron removed from the furnace at the end of the operation are called "puddle (puddled) balls," while the roughly elongated masses resulting from the squeezing of puddle balls are sometimes called "blooms." The blooms are rolled into "muck bars," or "puddle (puddled)" bars. The product resulting from the cutting, piling, heating, and rolling of muck bars is known as "refined iron," "refined bar," "merchant bar," "single rolled iron," "single refined iron," or "No. 2 iron"; if subjected to a second piling, heating, and rerolling, as "double (doubly) refined iron," "double rolled iron," "No. 3 iron," "best bar," "wire iron," or also "refined bar." (H. P. Tiemann.)

Wrought iron contains, besides an appreciable amount of slag, a small proportion of carbon and small quantities of the usual impurities, manganese, silicon, phosphorus, and sulphur.

Microstructure of Longitudinal Section. — Upon being withdrawn from the puddling furnace, the white-hot, pasty balls of wrought iron are subjected to vigorous forging or squeezing, thus expelling a large amount of slag and firmly welding to-

gether the particles of iron. Through additional heating and forging or rolling the metallic mass is converted into such elongated shapes as blooms, billets, bars, etc. These operations so affect the structure as to impart unlike appearances to sections cut longitudinally, i.e. in the direction of forging or rolling, and sections cut transversally, i.e. at right angles to that direction. The microstructure of the longitudinal section of a wrought-iron bar is shown in Figures 37 and 38. From our knowledge of the chemical composition of wrought iron we should be able to anticipate its microstructure. The ground mass or matrix of the metal consists of polyhedral crystalline grains of iron, that is of ferrite, similar in every respect to the crystalline grains of pure iron and of pure metals in general described in Chapters I and III. The ferrite of wrought iron, however, as explained in Chapter III, is not pure iron

Fig. 39. — Wrought iron. Transverse section. Magnification not stated. (Longmuir.)

Fig. 40. — Wrought iron. Transverse section. Magnified 250 diameters. (R. H. Greaves and Harold Wrighton.)

but rather a solid solution of iron in which are dissolved small quantities of silicon, phosphorus, and other minor impurities. This true character of commercial ferrite is too often lost sight of and the constituent considered as pure iron. The difference in coloration between adjacent grains of this commercial ferrite should be noted, and will of course be readily understood in view of the explanation given in Chapter I to account for this phenomenon. Many irregular black lines, varying much in thickness and length, but all running in the same direction, are clearly seen. These lines indicate the location of the slag which has assumed the shape of fibers or streaks running in the direction of the rolling or forging, thus imparting a fibrous *appearance* to the metal.

The presence of a small amount of carbon in wrought iron results in the occurrence of another constituent in the shape of small dark particles located between some of the grains. Under low magnification these carbon-holding particles are not readily distinguishable from slag particles. This carburized constituent, known as pearlite, which is not a very important one in the case of wrought iron, will be described in the next chapter. Summing up, wrought iron consists essentially of a mass of ferrite containing many elongated particles of slag.

Microstructure of Transverse Section. — The microstructure of the transverse

section of a wrought-iron bar is illustrated in Figures 39 and 40. Like the structure of the longitudinal section, it consists of a polygonal network, indicating that the metal is made up of polyhedral crystalline grains of ferrite. The slag, however, which in the longitudinal section occurred as fibers running in a direction parallel to the

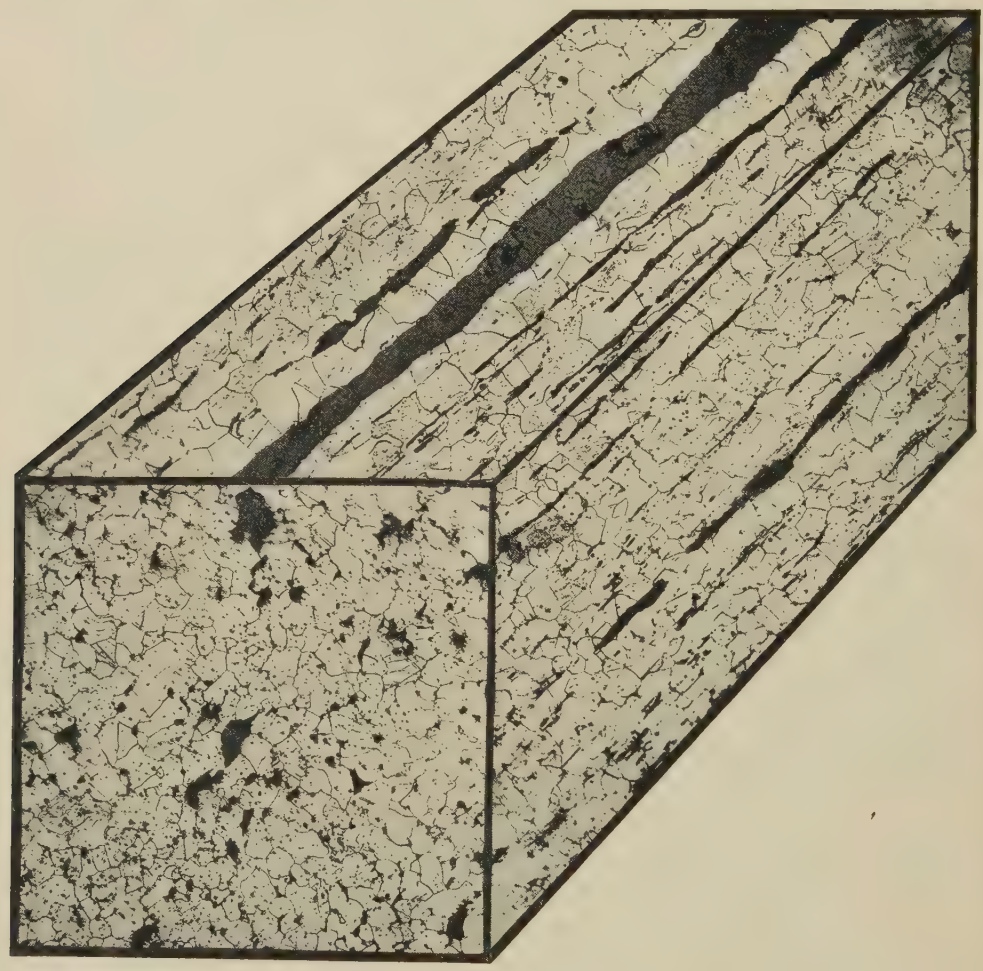


Fig. 41. — Wrought iron.

rolling or forging, here assumes the shape of irregular dark areas, corresponding to the cross sections of the slag fibers. It will be noted that in both the longitudinal and transverse sections the ferrite grains are equi-axed, that is they show no sign of having been elongated in the direction of the rolling. It was thought for many years that wrought iron actually had a fibrous structure, and indeed the number of persons still holding this view is surprisingly large. Many valuable properties were attributed to puddled iron on account of its "fibrous structure," which were denied to steel because of its "crystalline structure." The microscope has summarily disposed of this erroneous belief in showing that the ferrite constituting the bulk of wrought iron is in no way different from the ferrite forming the bulk of low carbon steel. Both are equally crystalline.

A "three dimensions" photomicrograph of wrought iron is shown in Figure 41. This was obtained by taking two photomicrographs longitudinally but at right angles to each other, and one transversally.

Structural Differences between Various Kinds of Wrought Iron. — According to W. Campbell, charcoal hearth iron can sometimes be distinguished from puddled iron through the presence in the former of bands of ferrite containing more or less pearlite (the carburized constituent of steel soon to be described), especially in their centers. The occurrence of these bands is ascribed to the carburizing of the iron by the glowing charcoal during the process of manufacture. Fagoted iron also contains ferrite and pearlite bands from the steel scrap used in its production but in these the pearlite does not decrease from center to outside, sharp lines of division existing between the bands and the ferrite matrix of the iron. It is difficult to distinguish between the

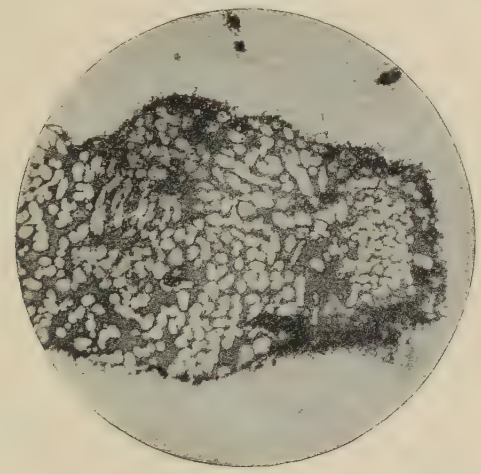


Fig. 42. — Particle of slag in wrought iron. Magnified 200 diameters. (Guillet.)

structure of busheled iron and that of puddled iron on the one hand and of charcoal iron on the other; when ferrite-pearlite bands occur in busheled iron they resemble those present in charcoal iron, while in the absence of such bands the structure resembles that of puddled iron.

Chemical Composition of Slag. — The essential chemical constituents of the slag produced in the puddling furnace and retained in part by the iron are iron oxides, both ferric (Fe_2O_3) and ferrous (FeO), oxide of manganese (MnO), silica (SiO_2), and phosphoric acid (P_2O_5). Of these the oxides of iron and manganese are basic in their chemical affinity while silica and phosphoric acid are acid. These bases and acids combine with each other to form neutral compounds: silicates and phosphates of iron and manganese.

Microstructure of Slag. — When highly magnified (Fig. 42) it is generally found that the slag fibers are really made up of at least two constituents, a dark and a lighter one, the light constituent moreover often occurring in the form of small rounded areas. We are naturally led to speculate as to the nature of these two distinct constituents of the slag, and in view of our knowledge of the chemical composition of slag as stated in the preceding paragraph we are tempted to conclude that one of the

constituents is a silicate of iron and manganese while the other is a phosphate of the same bases. The accuracy of this deduction, however, remains to be proven.

According to Matweieff the rounded light areas consist of iron oxide mixed or not with manganese oxide, and the darker background of silicate of iron and manganese.

Matweieff recommends the following method to distinguish between the different constituents of slag. The polished sample placed in a tube is heated and treated by a current of pure hydrogen, which causes the reduction of the metallic oxides while the silicates are unaffected. To detect the presence of ferrous oxide (FeO) the sample heated to a red heat is acted upon by steam, a treatment resulting in oxidizing the ferrous oxide into magnetic oxide (Fe_3O_4), while the silicates again remain unaltered. To detect the presence of manganese in the particles of oxides revealed by the hydrogen treatment the previously treated sample is repolished and etched with a dilute solution of ferric chloride in alcohol: if the white metallic grains resulting from the hydrogen treatment are colored darker than the surrounding iron they contain some manganese. Finally to detect the presence of iron and manganese sulphide the polished sample is etched with a dilute solution of tartaric acid, which colors sulphide of manganese lightly and iron sulphide decidedly.

Rosenhain considers it probable that the two distinct constituents of wrought-iron slag are two different silicates or, possibly, oxides of iron.

It is seen that writers generally ignore the presence of phosphoric acid in the slag from the puddling furnace, and still it generally contains from 3 to 5 per cent of it, and occasionally considerably more. If we assume that this phosphoric acid forms with iron a phosphate of the formula $3\ FeO{\cdot}P_2O_5$, a simple calculation, according to atomic weights of the elements involved, will show that the presence of 5 per cent of phosphoric acid would mean the formation of over 12.50 per cent of this phosphate of iron. It is hardly to be supposed that this phosphate is absorbed by some other constituent of the slag. On the contrary it seems highly probable that it must be present as a distinct constituent.

Influence of Thermal and Mechanical Treatments. — The dimensions of the ferrite grains of wrought iron are affected by the treatments, both thermal and mechanical, received by the metal. The effect of these treatments upon the structure of iron and steel will be considered in another chapter.

CHAPTER V

STEEL

In this chapter steel will be considered as a pure alloy of iron and carbon, i.e. free from the impurities (silicon, manganese, sulphur, and phosphorus) always present in commercial products. The influence of these elements upon the structure of steel will be dealt with separately.

Normal Structure.[1] — The structures described in this chapter refer to the condition of steel after forging followed by heating to, and slowly cooling from, a high temperature (900 to 1000 deg. C.). Such treatments, for reasons that will be understood later, promote soundness, remove internal strains, prevent excessive coarseness of structure (as in castings), and permit a state of stable equilibrium to be assumed by the constituents. The resulting structure may be conveniently called the "normal" structure and it will be so called in these pages.

Grading of Steel vs. Carbon Content. — Steel is generally graded according to the amount of carbon it contains. The following terms are those most commonly used:

Very low carbon steel, very mild, or extra mild steel, very soft or dead soft steel	carbon not over 0.10 per cent
Low carbon steel, mild steel, soft steel	carbon not over 0.25 per cent
Medium soft steel	carbon 0.26 to 0.40 per cent
Medium high carbon steel, half hard steel	carbon 0.41 to 0.60 per cent
High carbon steel, hard steel	carbon over 0.60 per cent
Very high carbon steel, very hard, or extra hard steel	carbon over 1.00 per cent

This classification is somewhat arbitrary as there are no sharp lines of demarcation universally recognized between the various grades.

It will be seen in another chapter that steel containing about 0.85 per cent carbon is also known as eutectoid steel, steel containing less carbon as hypo-eutectoid steel, and more highly carburized metal as hyper-eutectoid steel.

Low Carbon Steel vs. Wrought Iron. — As already mentioned the distinction between low carbon steel and wrought iron is generally based upon the difference between the methods employed for their respective manufacture rather than upon unlike chemical or physical properties, for these metals may indeed be quite identical

[1] It will be seen in Chapter XIII that the term "normalizing" is now frequently applied to a treatment consisting in heating steel above its thermal critical range followed by cooling *in air*, and it will also be shown that the steel may then be pearlitic or sorbitic or partly pearlitic and partly sorbitic in accordance with the dimensions of the pieces, and hence, with their rate of cooling. To have selected the term "normal" to describe their condition appears therefore unfortunate.

both physically and chemically. The mere melting of wrought iron would undoubtedly, in accordance with the universally accepted definition of steel, convert it into steel since we would now have a malleable metal *initially cast.* Such treatment would

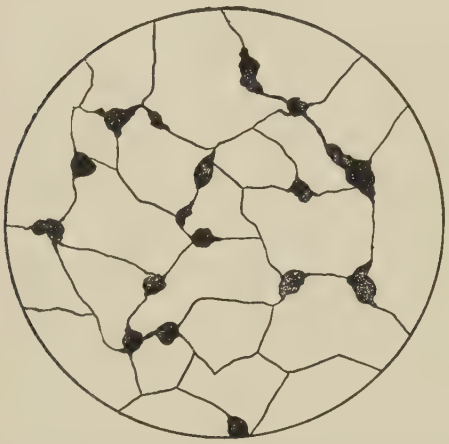


Fig. 43. — Steel. Carbon 0.08 per cent. Magnification not stated. (Arnold.)

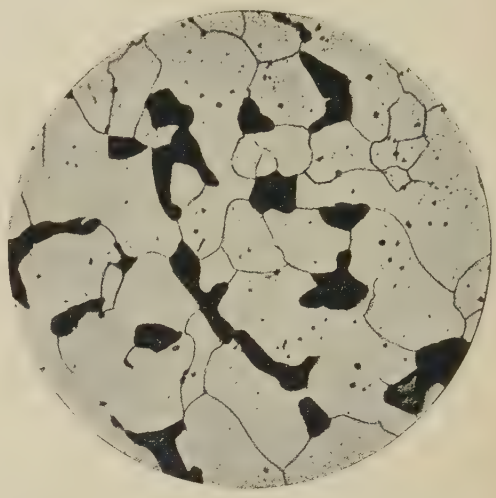


Fig. 44. — Steel. Carbon about 0.20 per cent. Magnified 200 diameters. (Guillet.)

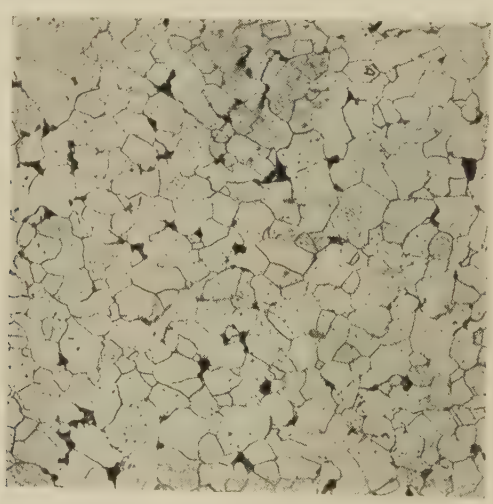


Fig. 45. — Steel. Carbon 0.10 per cent. Magnified 100 diameters. (E. L. Reed.)

of course result in the elimination of the slag mechanically retained by the wrought iron: the melted metal would be slagless, barring cemented steel, another essential property of steel. Since wrought iron generally contains but a small amount of carbon, melting it would convert it into low carbon steel. Were it practically free from carbon and manganese the remelted metal would be of the nature of ingot iron.

The Structure of Low Carbon Steel. — From the above considerations regarding the resemblance between wrought iron and low carbon steel, the structure of the

latter may be fairly anticipated. Seeing that low carbon steel may be considered as wrought iron from which the mechanically held slag has been expelled through melting, we should expect the absence of slag to be the only marked difference between the structure of low carbon steel and that of wrought iron.

The microstructure of low carbon steel is illustrated in Figures 43 to 48. It will be seen (Figs. 43 and 44) to consist chiefly of a mass of ferrite (carbonless iron) ex-

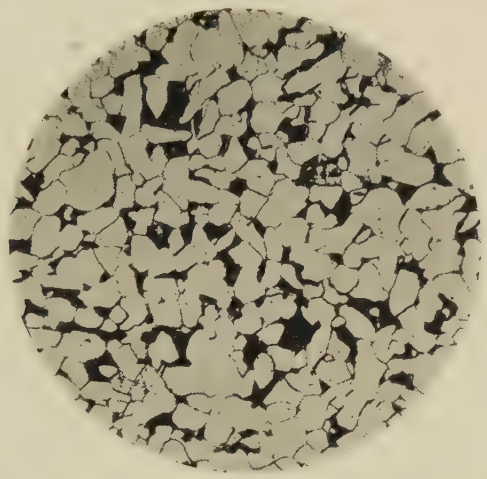


Fig. 46. — Steel. Carbon about 0.20 per cent.
(L. T. Holt, Correspondence Course student.)

hibiting the usual polyhedral crystalline grains described in preceding chapters. The ferrite present in low carbon steel is similar in every respect to the ferrite of wrought iron. At the junctions of many ferrite grains, however, some dark areas will be noted, an evidence of the existence in the metal of another constituent. Since ferrite is practically free from carbon, it is evident that the carbon present in the steel must have segregated into these small dark masses. As to the exact nature of this dark constituent it will be apparent that it cannot consist of pure carbon, for it is well known that the carbon present in steel does not exist in the free state but on the contrary is combined with some of the iron forming a definite chemical compound or carbide of iron whose formula is Fe_3C.[1] This iron carbide must necessarily be located in the dark areas, but are these made up exclusively of this carbide? To find an answer to this question let us examine the structure of steel under a higher magnification (Figs. 47 and 48). This reveals the existence of two components in each dark particle occurring as small wavy or curved parallel plates or lamellæ alternately dark and white. As to the nature of these two components, it is evident that one of them must be the carbide Fe_3C and the other necessarily iron or ferrite, since according to the proximate analysis of steel, these are the only two constituents which, to the best of our knowledge, are present in pure unhardened carbon steel.

Pearlite. — Howe named the microscopical constituent just described "pearlite"

[1] The existence of the carbide Fe_3C in unhardened steel was first shown in 1885 by Abel and Muller, working independently, and has since been confirmed by many other investigators. Its existence is proved by dissolving unhardened steel in a suitable solvent and analyzing the carbonaceous residue.

(originally written pearlyte), following in this Dr. Sorby, who was the first observer to describe it and who had proposed for it the name of "pearly constituent" because it frequently exhibits a display of colors very suggestive of mother-of-pearl, especially when viewed by oblique illumination. This appearance is due to the fact that these plates are extremely thin, seldom measuring over $\frac{1}{25000}$ of an inch in thickness, and that the plates of carbide, being much harder than the ferrite plates, stand in relief after polishing, resulting in an arrangement very similar to the refraction gratings of physicists. Mother-of-pearl likewise is made up of very thin alternate plates of dif-

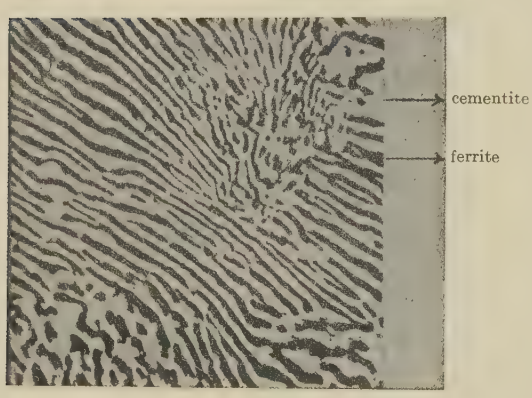


Fig. 47. — Steel. Structure of pearlite. Magnified 1000 diameters. (Osmond.)

Fig. 48. — Steel, hypo-eutectoid. Magnified 750 diameters. Pearlite particles and surrounding ferrite. (Gœrens.)

ferent colors and possibly of different hardness. The carbide plates remain bright, not being affected by the usual etching reagents, while the ferrite plates appear dark because of their being somewhat tarnished by the etching, and also because, being depressed owing to their greater softness, they stand in the shadow of the carbide plates. It will be shown in another chapter that in many series of alloys of two metals the alloy of lowest melting point, called the "eutectic" alloy, very frequently exhibits a composite structure like that of pearlite, i.e. made up of parallel plates alternately of one and the other constituents. It will also be shown that in spite of this very great structural resemblance pearlite is not a true eutectic alloy. Howe proposed to call "eutectoid" the kind of mechanical mixture found in pearlite and this most appropriate term has been universally adopted.

Because of the minute dimensions of the lamellæ of pearlite a high magnification, generally not less than 250 or 300 diameters, is required for its resolution.

Very high power photomicrographs of ferrite and pearlite, and of pearlite alone, of exceptional clearness, are shown in Figures 49 and 50 taken by F. F. Lucas.

It should be stated here that pearlite does not always assume such a distinctly laminated structure. In many instances its structure remains ill defined or has a granular rather than a lamellar appearance, while its behavior towards the etching

reagents likewise varies. It will be shown at the proper time that this is due to the treatments to which steel may be subjected and that the exact nature of these ill-defined forms of pearlite has given rise to a large amount of discussion and has been the object of many investigations. It may be assumed for the present that any pearlite which is not distinctly lamellar is not true pearlite.

Fig. 49. — Steel. Carbon 0.20 per cent. Magnified 2800 diameters. (F. F. Lucas.)

It will be noted that in Figure 44 the pearlite occupies about twice the area covered by the same constituent in Figure 43. We infer from this that the amount of pearlite in low carbon steel at least increases progressively with the carbon content. Doubling the amount of carbon doubles of course the proportion of the iron carbide in the steel, and since the amount of pearlite is apparently also doubled it follows that iron carbide and ferrite must unite with each other in fixed ratio to form pearlite, in other words that pearlite always contains the same proportion of carbide and hence also of carbon. The accuracy of this conclusion will soon be shown.

Free Ferrite. — To distinguish between the ferrite included in pearlite and the ferrite forming the balance of low carbon steel, the latter is sometimes called "free," "structurally free," "excess," "massive," "non-eutectoid," "pro-eutectoid," or "surplus" ferrite. In these pages it will be referred to as free ferrite, while the ferrite

Fig. 50. — Pearlite. Magnified 2800 diameters. (F. F. Lucas.)

forming part of the pearlite will be called pearlite-ferrite. Some writers refer to the latter as eutectoid-ferrite.

In the absence of any conclusive evidence to the contrary, it is natural to infer that free ferrite and pearlite-ferrite are identical, that is pure iron in pure steel and iron holding in solution small quantities of silicon and phosphorus, and possibly of other impurities, in impure (commerical) steel.[1]

[1] This has been doubted by some writers, however, who have noted that the ferrite of some pearlites was more readily colored on etching than free ferrite, and they saw in this and in some other

Cementite. — The name of cementite has been given by Howe to the carbide Fe_3C and universally adopted. The term is derived from "cement" steel (cementation steel, blister steel, converted steel), which being generally a high carbon steel contains a great deal of this carbide, that is of cementite.

According to the atomic weights of iron (assumed to be 56) and of carbon (12) cementite must contain

$$\frac{12 \times 100}{3 \times 56 + 12} = 6.67 \text{ per cent carbon}$$

The carbon present in cementite is frequently referred to as "cement" carbon, occasionally as carbide carbon, to distinguish it from other forms of carbon found in iron and steel and to be described later (hardening carbon, graphitic carbon, temper carbon, etc.).

Cementite is an extremely hard substance, being in fact the hardest of all the constituents occurring in iron and steel, harder even than hardened, high carbon steel. Howe states that it is harder than glass and nearly as brittle. As it scratches feldspar but not quartz it is generally assigned to rank 6.5 in the Mohs scale of hardness.[1]

It will be shown later that when steel contains an appreciable amount of manganese, as is always the case in commercial products, a portion at least of this manganese also forms a carbide Mn_3C and that this carbide unites with the iron carbide Fe_3C to form cementite. It is well to bear in mind, therefore, that in commercial steel cementite generally contains besides Fe_3C varying amounts of this carbide of manganese. As the atomic weight of manganese is nearly the same as that of iron, 55 compared to 56, it so happens that the presence of manganese in cementite affects but very little its carbon content, which for all practical purposes may be taken as 6.67 regardless of the amount of manganese it may contain. Cementite containing much manganese has been called manganiferous cementite by some writers.

Recent investigations tend to show that cementite may also contain small amounts of silicon and sulphur dissolved in it, possibly as silicide and sulphide of iron respectively, although Stead and W. H. Hatfield mentioned the presence of silicon carbide. It will be shown elsewhere that some of these elements (manganese and sulphur) apparently increase the stability of cementite while silicon decreases it.

Baykoff has advanced the theory that cementite is not a definite compound or mixture of definite compounds but a solid solution.

Cementite generally remains bright and brilliant after the ordinary etching treatments employed to reveal the structure of steel. Sodium picrate, however, colors it deeply (see Appendix II).

Medium High Carbon Steel. — The normal structure of steel (i.e. its structure after working, reheating to a high temperature, and slow cooling) containing about 0.30 per cent carbon is illustrated by a drawing in Figure 51 and by a photomicrograph in Figure 52. It will be noted, on comparing this structure with that of lower

evidences an indication that pearlite-ferrite may be less pure than free ferrite. Benedicks for instance believes, or at least believed at one time, that the pearlite-ferrite of some steels could contain as much as 0.27 per cent of carbon dissolved in beta iron, whereas free ferrite is in the alpha condition. This carburized and allotropic ferrite Benedicks called "ferronite."

[1] The Mohs scale is as follows, beginning with the softest and ending with the hardest mineral, and each mineral being capable of scratching the preceding ones: (1) Talc, (2) Gypsum, (3) Calcite, (4) Fluorite, (5) Apatite, (6) Feldspar, (7) Quartz, (8) Topaz, (9) Corundum, and (10) Diamond.

carbon steels, that the introduction of more carbon in the iron has resulted, as would be expected, in the occurrence of a greater amount of pearlite and of a correspondingly smaller proportion of ferrite. The pearlite occupies now roughly about one third of the total area. The junction lines between the grains of ferrite should be noted.

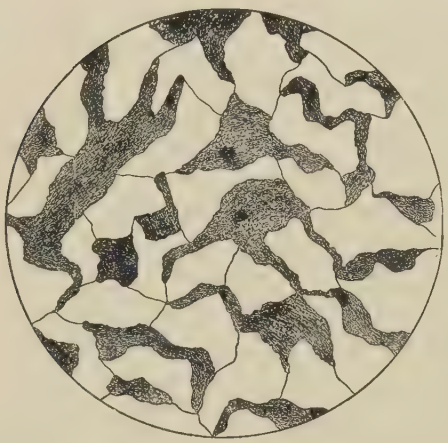


Fig. 51. — Steel. Carbon 0.38 per cent. Magnification not stated. (Arnold.)

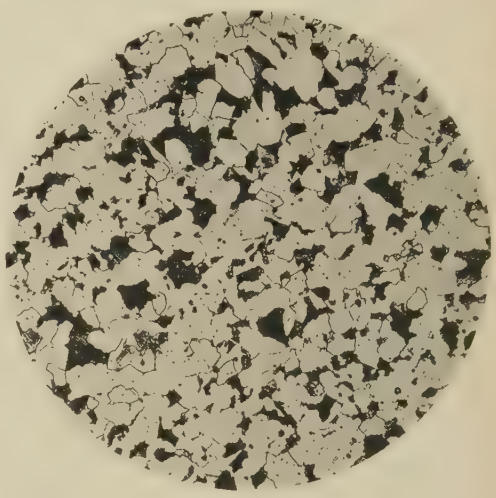


Fig. 52. — Steel. Carbon 0.30 per cent. Magnified 150 diameters. Forged and annealed. (C. C. Buck, Correspondence Course student.)

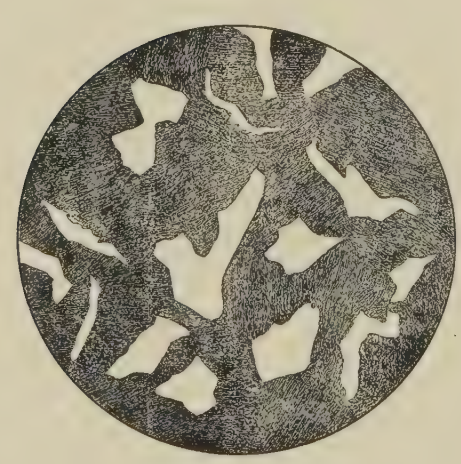


Fig. 53. — Steel. Carbon 0.59 per cent. Magnification not stated. (Arnold.)

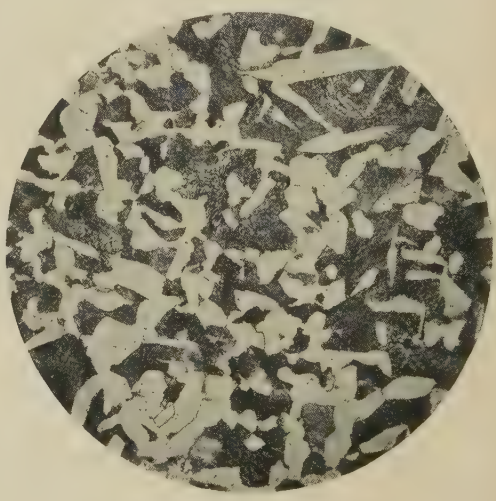


Fig. 54. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and slowly cooled in furnace. (Burger.)

Under sufficiently high power the pearlite areas exhibit the characteristic lamellar structure previously described.

On further addition of carbon, the amount of pearlite, which is evidently proportional to the percentage of carbon, increases correspondingly, as shown in Figures 53

and 54 illustrating the microstructure of steel containing about 0.50 per cent carbon. The pearlite occupies here over one half of the total area. It will be noticed that the ferrite areas are only occasionally resolved into polyhedral grains, apparently because the ferrite now occurs in particles often too small to be made up of several crystalline grains. These small masses of ferrite, however, are still made up of crystalline matter, as described and illustrated in Chapter III. A high power photomicrograph of 0.45 per cent carbon steel is shown in Figure 55. The laminations of pearlite are clearly seen.

When steel contains but a small, although appreciable, amount of ferrite, as is the case with carbon contents between 0.50 and 0.70 per cent, the ferrite frequently forms envelopes or membranes surrounding the pearlite grains, an arrangement generally described as a network structure, the pearlite forming the meshes and the

Fig. 55. — Steel. Carbon 0.45 per cent. Magnified 1000 diameters. (Osmond.)

free ferrite the net proper. These pearlite meshes are also described as "cells" or "kernels" and the ferrite membranes as "cell walls" or "shells."

It will be shown later that this network structure is promoted by rather rapid cooling from a high temperature, as for instance by cooling small pieces in air.

Structures of this type are illustrated in Figures 56 and 57. The latter illustration is of special interest, being a reproduction of one of Sorby's original drawings and, therefore, the first drawing of pearlite ever published.

High Carbon Steel. — Since the introduction of increasing amounts of carbon in steel results in the formation of a correspondingly increasing proportion of pearlite and a decreasing proportion of ferrite, a degree of carburization must necessarily be reached when the whole mass will be made up of pearlite, the ferrite having finally disappeared. This critical point in the structure of steel is attained when the metal

contains somewhere between 0.80 and 0.90 per cent of carbon, exceptionally pure steel requiring the larger proportion of carbon and impure steel the smaller for the complete disappearance of ferrite.

Fig. 56. — Hypo-eutectoid steel. Magnified 100 diameters. (Ford Motor Co., Correspondence Course class.)

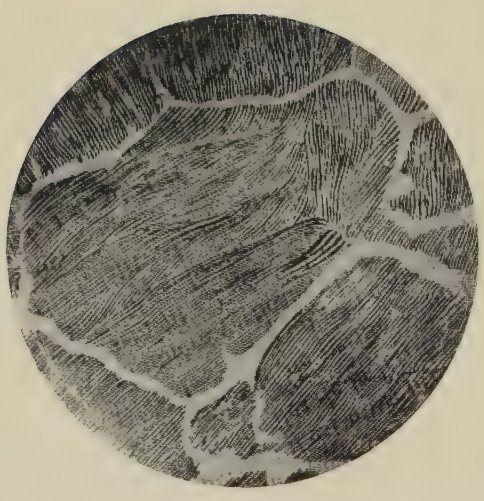


Fig. 57. — Steel, hypo-eutectoid. (Sorby.)

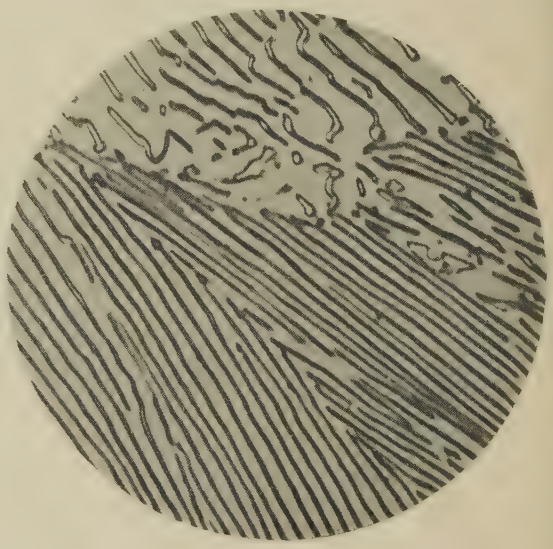


Fig. 58. — Eutectoid steel. Magnified 1000 diameters. (K. W. Grant, Correspondence Course student.)

Eutectoid Steel. — Steel made up exclusively of pearlite is now quite universally called "eutectoid" steel, after Howe, the name suggesting the great resemblance between pearlite and eutectic alloys, while at the same time clearly indicating that pearlite is not a true eutectic alloy. Previous to Howe's happy suggestion this steel

was commonly described as "eutectic" or "saturated" steel. It has also been termed "aeolic" or "benmutic" steel by Howe, but these names have now been abandoned. The structure of eutectoid steel is illustrated in Figure 58, and under a magnification in Figure 59.

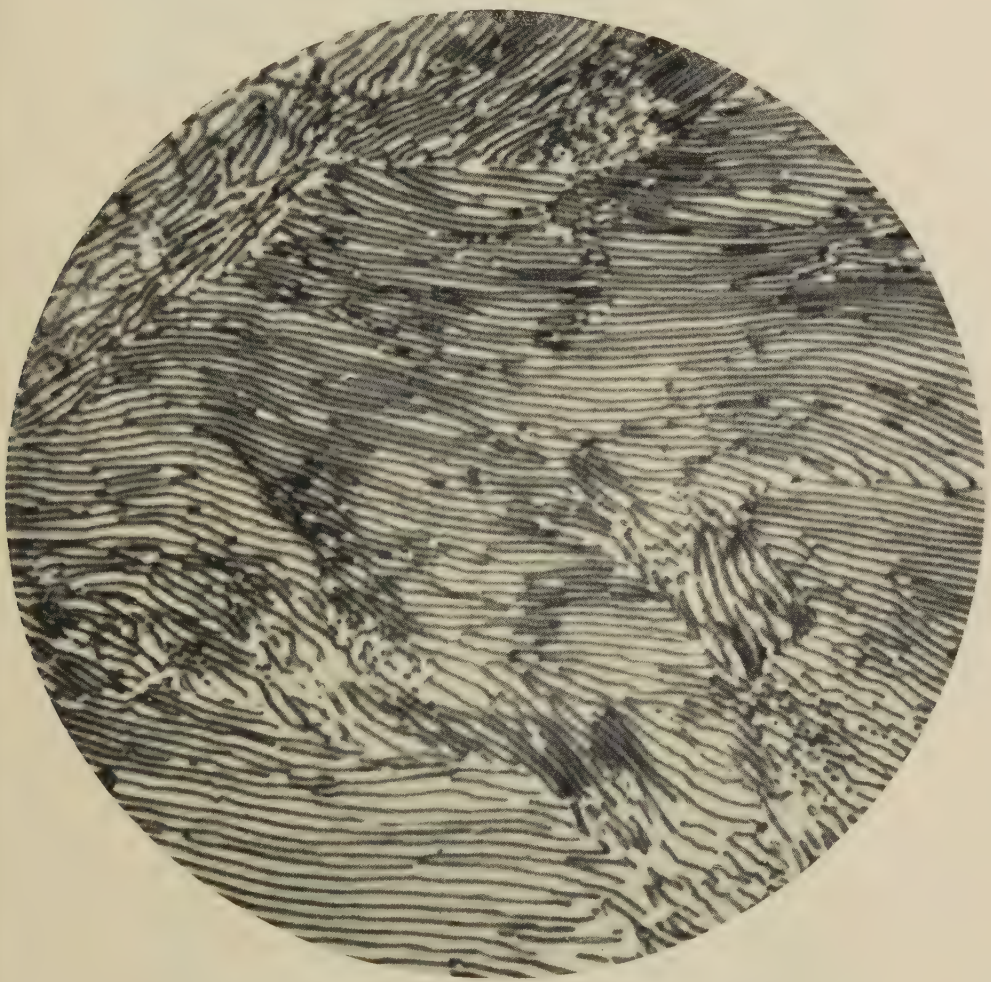


Fig. 59. — Eutectoid steel. Magnified 2800 diameters. (F. F. Lucas.)

Steel containing less than 0.85 per cent carbon or thereabout, and in which, therefore, some free ferrite is present, is called "hypo-eutectoid," while steel more highly carburized than eutectoid steel is called "hyper-eutectoid." It will be shown presently that hyper-eutectoid steel contains free cementite.

Hyper-Eutectoid Steel. — The normal structure of steel containing from 1.10 to 1.50 per cent carbon is illustrated in Figures 60 to 63 both under low and high magnification. These steels will be seen to consist, like hypo-eutectoid steel, of two constituents, one of which is pearlite, as clearly shown when examined under high power. The other constituent remains bright after etching and might at first be taken for ferrite. Upon reflection, however, it will be evident that such cannot be its

nature. The light constituent of hyper-eutectoid steel consists of cementite, which is now present in excess over the amount required to form pearlite, just as in hypo-eutectoid steel ferrite is the excess constituent. It will be evident that the ferrite

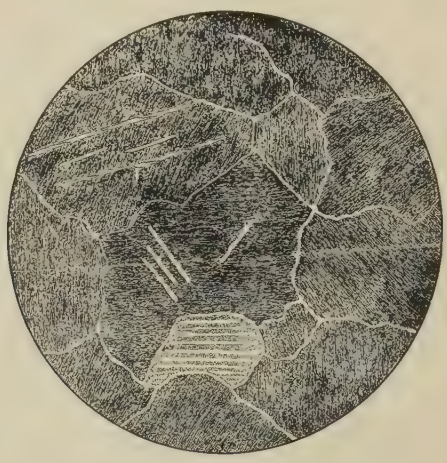


Fig. 60. — Steel. Carbon 1.20 per cent. Magnification not stated. (Arnold.)

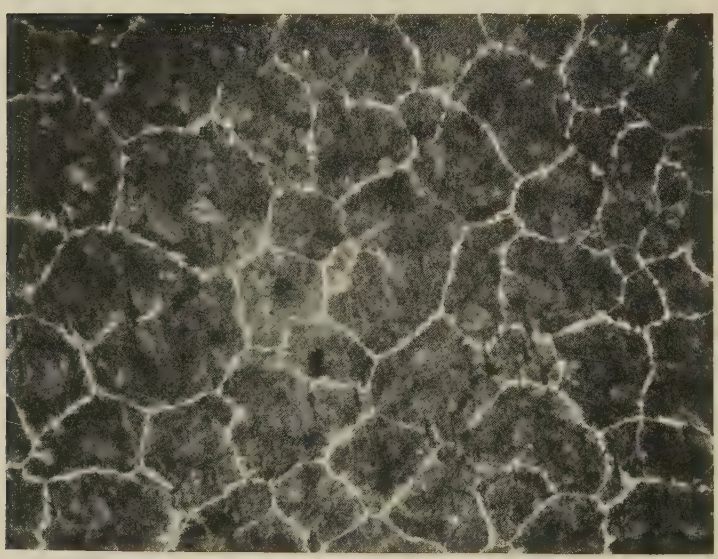


Fig. 61. — Steel. Carbon 1.10 per cent. Magnified 100 diameters. (Boynton.)

and cementite which constitute all grades of carbon steels combine with each other in suitable proportions to form pearlite, leaving, as the case may be, an excess of ferrite (in hypo-eutectoid steel) or of cementite (in hyper-eutectoid steel).

A more scientific explanation of the formation of the normal structure of steel will be offered in a subsequent chapter.

Free Cementite. — To distinguish between the cementite forming part of the

pearlite (the bright plates of that constituent) and the cementite constituting the balance of hyper-eutectoid steel, the latter is generally called "free," "structurally

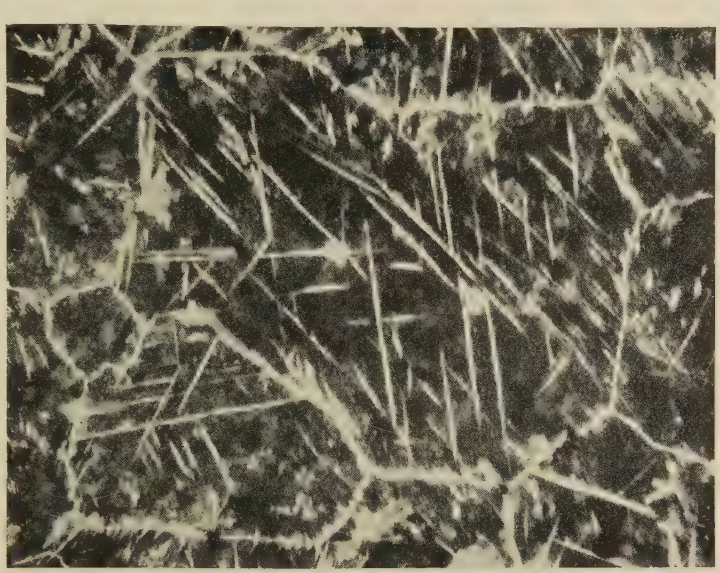


Fig. 62. — Steel. Carbon 1.43 per cent. Magnified 50 diameters. (Boynton.)

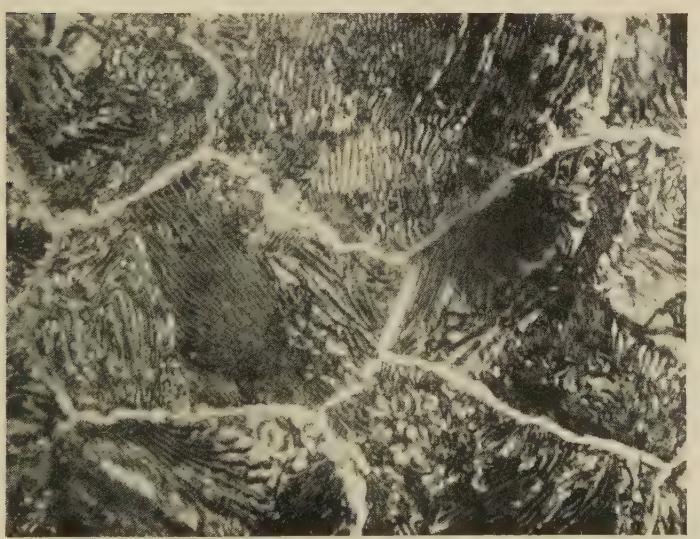


Fig. 63. — Steel. Carbon 1.43 per cent. Magnified 500 diameters. (Boynton.)

free," "excess," "massive," "non-eutectoid," or "surplus" cementite, while the cementite included in the pearlite is sometimes referred to as pearlite-cementite or eutectoid-cementite. In these pages the cementite in excess over the eutectoid ratio will be called free cementite.

In the absence of any conclusive evidences to the contrary, and in conformity

with the nature of eutectic alloys in general, it is assumed that free cementite and pearlite-cementite are identical in composition and properties.

As already stated, the cementite of commercial steel is not pure Fe_3C but contains small and varying amounts of Mn_3C, and possibly also a little silicon and sulphur.

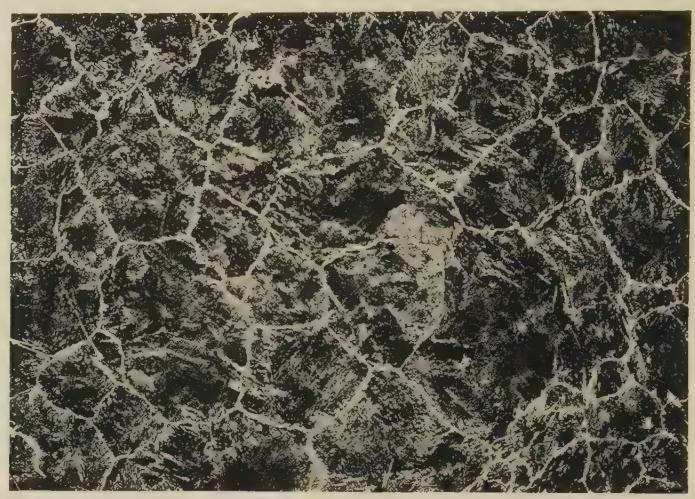


Fig. 64. — Steel, hyper-eutectoid. Etched with nitric acid. Cementite uncolored, pearlite colored. Magnified 100 diameters. (R. W. Smyth, in the author's laboratory.)

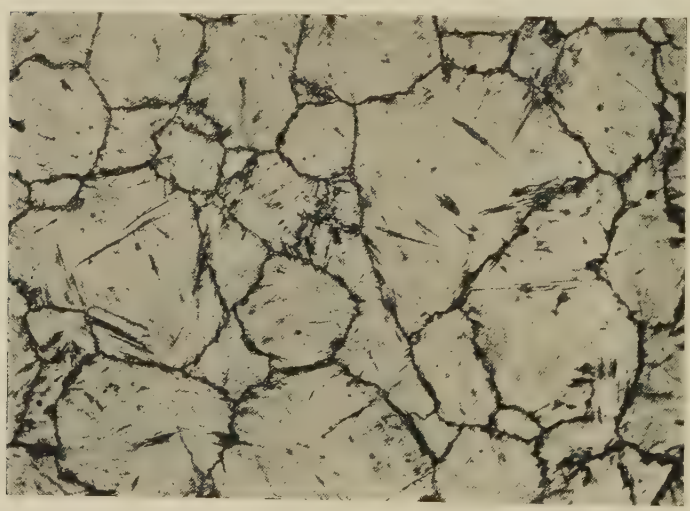


Fig. 65. — Same as Fig. 64. Etched with sodium picrate. Cementite colored dark, pearlite uncolored. (R. W. Smyth, in the author's laboratory.)

As shown in Figures 60 and 61 hyper-eutectoid steel like hypo-eutectoid steel may assume a network structure. In both cases the meshes consist of pearlite but the net proper, which in hypo-eutectoid steel represents membranes of free ferrite, indicates now the occurrence of membranes of free cementite.

Hypo- vs. Hyper-Eutectoid Steel. — While there is considerable similarity between the structure of steel containing but a slight excess of ferrite and the structure of steel containing but a slight excess of cementite, a little experience and careful examination will reveal differences in their appearances and properties which will make it possible, generally, to distinguish between them. Cementite has a more metallic luster than ferrite and remains bright and structureless, even after prolonged etching with the ordinary reagents, while ferrite is colored and, if present in sufficiently large masses, resolved into grains by such treatment. Cementite is extremely hard, standing in relief, while ferrite being soft is depressed by the polishing operation. Ferrite is readily scratched by a needle drawn across the polished surface, while cementite remains unmarked.

When cementite is in excess the pearlite grains are generally smaller and the network finer than is the case with excess of ferrite. Free cementite does not, of course, always assume the shape of a fine network. It will be shown in subsequent chapters that its mode of occurrence depends upon the treatment to which the steel was subjected.

Etching of Cementite. — It has been seen that cementite is not acted upon by the usual reagents employed in the etching of steel sections (picric acid, nitric acid, tincture of iodine, etc.) but that it is darkly colored by a suitable treatment with sodium picrate, while pearlite on the contrary remains bright.

In Figures 64 and 65 is shown the structure of the same specimen of hyper-eutectoid steel etched respectively with nitric acid and with sodium picrate.

Carbon Content of Pearlite. — The percentage of carbon in pearlite and, therefore, in eutectoid steel, has been stated to be somewhere between 0.80 and 0.90 in commercial steel of ordinary quality because when steel of that degree of carburization is examined under the microscope it is found to be free from any appreciable amount of free ferrite or of free cementite. As the presence of a very small amount of any of these two constituents in the free state, however, is very difficult to ascertain, it will be evident that it is quite impossible to speak positively as to the exact amount of carbon needed to exclude both free ferrite and free cementite from the structure. Moreover this carbon content of pearlite varies somewhat with the composition of the steel and with the treatment it has received. In steel of ordinary commercial purity the eutectoid point appears to be in the vicinity of 0.85 per cent carbon.

Structural Composition of Steel. — Since the atomic weight of carbon is 12, and assuming the atomic weight of iron to be exactly 56, it follows, as already stated, that the carbide Fe_3C or cementite contains 6.67 per cent carbon.

It also follows that one part of carbon in the steel will produce

$$\frac{3 \times 56 + 12}{12}$$

or exactly 15 parts of cementite. If the steel contains 1 per cent carbon, for example, it will contain 15 per cent cementite; with 0.50 per cent carbon it will contain 0.50×15, or 7.5 per cent cementite, and so on.

Assuming the percentage of carbon in pearlite to be 0.85 per cent, that constituent will contain 0.85×15, or 12.75 per cent cementite, and necessarily, $100 - 12.75 = 87.25$ per cent ferrite, or

$$\frac{87.25}{12.75} = 6.8$$

parts of ferrite by weight for each part of cementite. Again, one part of cementite will produce

$$\frac{100}{12.75} = 7.8 \text{ of pearlite}$$

Since in hypo-eutectoid steel the entire amount of carbon present is included in the pearlite, the structural composition may readily be calculated. It will contain:

$$C \times 15 \times 7.8 = C \times 117 \text{ per cent pearlite}$$

in which C represents the carbon content. To calculate the structural composition of any hypo-eutectoid steel it suffices, therefore, to multiply its carbon content by 117 in order to obtain the percentage of pearlite. The balance is necessarily free ferrite. Steel containing 0.50 per cent carbon, for example, will consist of

$$0.50 \times 117 = 58.50 \text{ per cent pearlite and}$$
$$100 - 58.50 = 41.50 \text{ per cent free ferrite}$$

It should be remembered that the structure of steel now under consideration is what has been termed its "normal" structure; it is assumed that the metal has cooled slowly from a temperature higher than its critical range, as later explained, or, to express it differently, that the steel has been made pearlitic.

Hyper-eutectoid steel contains both pearlite and free cementite, the former constituent containing 0.85 per cent C and the latter 6.67 per cent carbon. If x and y represent respectively the percentages of pearlite and free cementite present in the steel, and C the known percentage of carbon, we may write the following equations:

$$(1) \quad x + y = 100$$
$$(2) \quad \frac{0.85}{100}x + \frac{6.67}{100}y = C$$

the first term of the second equation representing the amount of carbon in the pearlite, and the second the amount of carbon in the free cementite. The sum of the two is necessarily equal to the carbon in the steel. Solving these equations we obtain:

$$x = \frac{667 - 100\,C}{5.82}$$

or approximately

$$x = 115 - 17\,C$$

To obtain the percentage of pearlite present in hyper-eutectoid steel it suffices, therefore, to multiply the carbon content by 17 and to subtract the result from 115. The balance of the steel is necessarily free cementite. Or using another method: $C \times 15$ represents the total amount of cementite in the steel, hence $100 - (C \times 15)$ represents the total ferrite present. In hypereutectoid steel, all the ferrite is included in the pearlite, and since 1 part of ferrite produces

$$\frac{100}{87.25} = 1.15 \text{ parts of pearlite}$$

the steel will contain $(100 - C \times 15) \times 1.15 = 115 - 17.25\,C$ per cent of pearlite. Steel containing 1.25 per cent carbon, for instance, will be made up of

$$115 - (17 \times 1.25) = 93.75 \text{ per cent pearlite, and}$$
$$100 - 93.75 = 6.25 \text{ per cent of free cementite.}$$

Chemical vs. Structural Composition. — Disregarding for the present the existence of impurities, the ultimate chemical analysis of steel reveals the presence of so much carbon and so much iron. The proximate chemical analysis of steel reveals (in steel slowly cooled from a high temperature) the presence of so much iron and so much carbide of iron, Fe_3C. In a similar way we may consider two different structural compositions, an ultimate and a proximate one. The ultimate structural composition reveals the presence of so much total ferrite and so much total cementite, while the proximate structural composition informs us of the percentages of pearlite, free ferrite, and free cementite in the steel. It will be evident that the chemical proximate composition is identical to the ultimate structural composition, the names of the

CHEMICAL COMPOSITION		STRUCTURAL COMPOSITION				
Ultimate		Ultimate		Proximate		
C	Fe	Total Cementite	Total Ferrite	Pearlite	Free Ferrite	Free Cementite
.1	99.9	1.5	98.5	11.7	88.3	—
.2	99.8	3.0	97.0	23.4	76.6	—
.3	99.7	4.5	95.5	35.1	64.9	—
.4	99.6	6.0	94.0	46.8	53.2	—
.5	99.5	7.5	92.5	58.5	41.5	—
.6	99.4	9.0	91.0	70.2	29.8	—
.7	99.3	10.5	89.5	81.9	18.1	—
.8	99.2	12.0	88.0	93.6	6.4	—
.9	99.1	13.5	86.5	99.7	—	0.3
1.0	99.0	15.0	85.0	98.0	—	2.0
1.1	98.9	16.5	83.5	96.3	—	3.7
1.2	98.8	18.0	82.0	94.6	—	5.4
1.3	98.7	19.5	80.5	92.9	—	7.1
1.4	98.6	21.0	79.0	91.2	—	8.8
1.5	98.5	22.5	77.5	89.5	—	11.0
1.6	98.4	24.0	76.0	87.8	—	12.2
1.7	98.3	25.5	74.5	86.1	—	13.9
1.8	98.2	27.0	73.0	84.4	—	15.6
1.9	98.1	28.5	71.5	82.7	—	17.7
2.0	98.0	30.0	70.0	81.0	—	19.0

Carbon	Hypo-Eutectoid Steel	Hyper-Eutectoid Steel
%	Values to be added to % of pearlite and subtracted from % ferrite	Values to be subtracted from % pearlite and added to % cementite
0.01	1.17	0.17
0.02	2.34	0.34
0.03	3.51	0.51
0.04	4.68	0.68
0.05	5.85	0.85
0.06	7.02	1.02
0.07	8.19	1.19
0.08	9.36	1.36
0.09	10.53	1.53

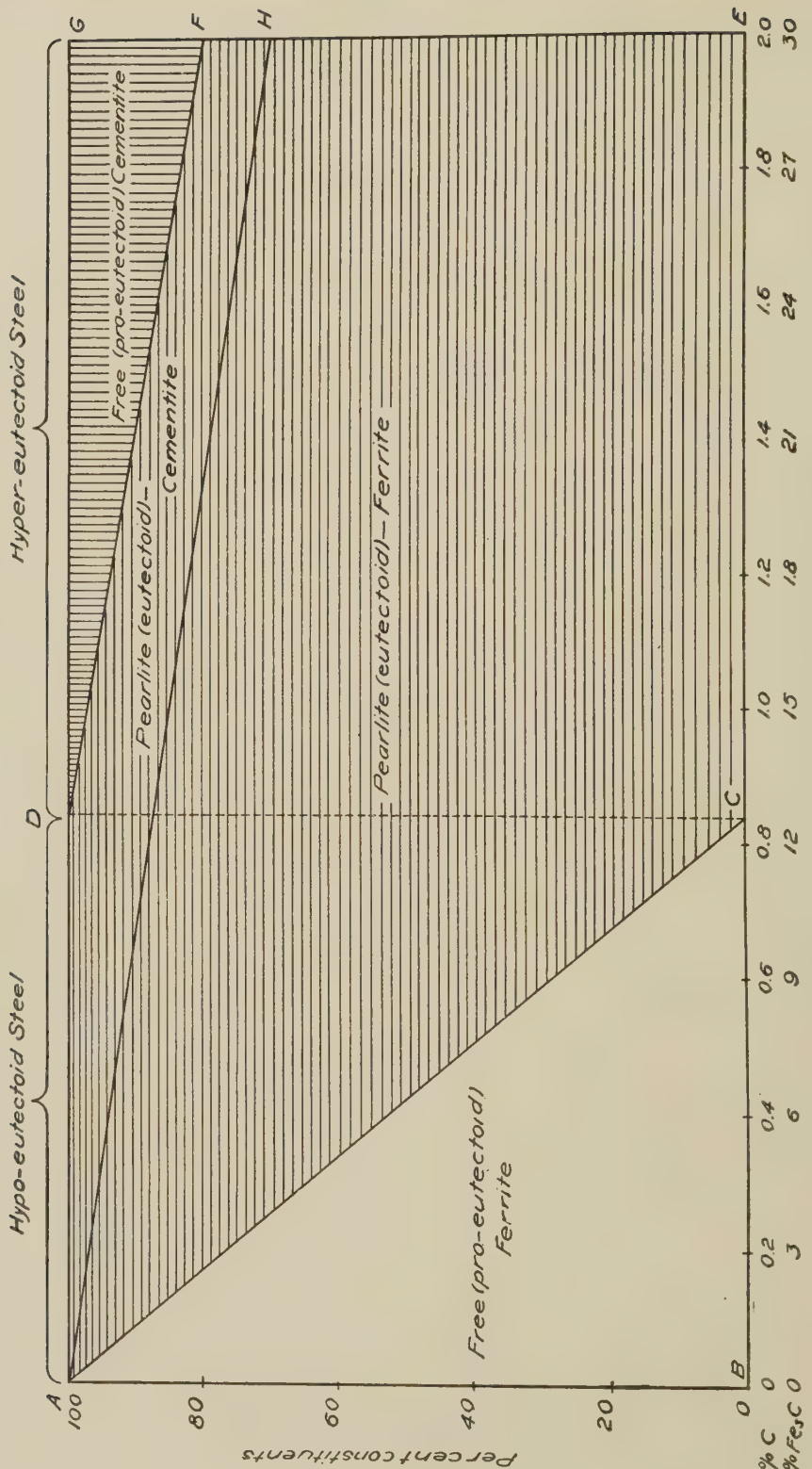


Fig. 66. — Diagram of the structural composition of slowly cooled carbon steels.

constituents only being different, iron and carbide in the first case, ferrite and cementite in the latter. These various compositions are tabulated below:

		Constituents		
Chemical Composition	ultimate	Fe	C	
	proximate	Fe	Fe_3C	
Structural Composition	ultimate	total ferrite	total cementite	
	proximate	pearlite	free ferrite	free cementite

It is apparent that the proximate structural composition affords more valuable information than is obtainable through the other three kinds of analysis, for not only does it indicate the chemical nature of the proximate constituents but also their structural association and occurrence, upon which depend, to a very great extent, the physical properties of steel. In the first table on page 63 the ultimate chemical composition as well as the structural composition, both ultimate and proximate, of steel containing from 0.1 to 2.0 per cent of carbon, have been calculated for each increase of carbon of 0.1 per cent. Corrections for variations of 0.01 per cent carbon can readily be obtained by interpolation and are indicated in the second table on page 63.

These compositions are shown also diagrammatically in Figure 66, which will be readily understood. ABC represents the free ferrite in hypo-eutectoid steel, ACD the pearlite in hypo-eutectoid steel, DCEF the pearlite in hyper-eutectoid steel, DFG the free cementite in hyper-eutectoid steel, ABEH the total ferrite in any steel, AHG the total cementite in any steel, ACEH the pearlite-ferrite in any steel, and AHFD the pearlite-cementite in any steel.

Micro-Test for Determination of Carbon in Steel. — Since the amount of pearlite in steel is proportional to the percentage of carbon it contains, it should be possible to estimate the latter with a fair degree of accuracy from the area occupied by the pearlite. After a little experience and by taking the necessary precautions it will be found that, in the case of decidedly hypo-eutectoid steels at least (steels containing say less than 0.60 per cent carbon), results are obtained quite as accurate as those of the calorimetric method and, on the whole, more reliable, since the possibility of serious errors is practically eliminated.

In order to yield results at all satisfactory, however, care should be taken that all samples be first annealed, that is reheated to 900 or 1000 deg. C. and cooled slowly, so that the normal amounts of pearlite may be formed. To attempt to apply the micro-test to forged unannealed samples, for instance, is certain to lead to failure. Nor can the test be applied to hypo-eutectoid steel containing but a slight amount of free ferrite, for instance to steel with from 0.60 to 0.80 per cent carbon, because of the difficulty of estimating accurately the area occupied by so small a proportion of the constituent in excess, and therefore by the pearlite itself. In the case of hyper-eutectoid steel, the differences between the contents of free cementite in steels of materially different carbon contents is so small as to resist accurate determination. For instance, steels respectively with 1.10 and 1.40 per cent carbon will contain 96.3 and 91.2 per cent pearlite, a difference of less than 5 per cent, too small to be estimated with satisfactory accuracy under the microscope.

The author has found the following method to yield in some instances satisfactory results: the sample after annealing and quick polishing and etching (a few small polishing scratches will not matter) is placed under the microscope, using a 16 mm. objective and a 5X eyepiece, and its image thrown on the screen of the camera. In

place of the ordinary camera screen, however, another screen is substituted of ground glass, ruled into 81 squares (9 × 9), so that every square covered by pearlite evidently means very nearly 0.01 per cent of carbon in the steel (exactly 0.01 per cent carbon if we assume pearlite to contain 0.81 per cent carbon). It is then sufficient to estimate the number of squares occupied by pearlite to arrive at the carbon content of the steel. The result may be checked by estimating the carbon in two or more different spots and reporting the average if the agreement is sufficiently close.

Physical Properties of the Constituents of Steel. — It will now be timely and profitable to inquire into the physical properties of the three constituents, ferrite, cementite, and pearlite, of which steel in its normal condition is composed.

It will be evident that the physical properties of commercial ferrite must resemble closely those of wrought iron and of very low carbon steel. Ferrite, therefore, is very soft, very ductile, and relatively weak, having a ductility corresponding to an elongation of at least 50 per cent in 2 inches, and a tensile strength of some 40,000 pounds per square inch. It is magnetic, has a high electric conductivity, high permeability, low residual magnetism, and is deprived of hardening power, industrially speaking at least, since carbonless iron cannot be materially hardened by rapid cooling from a high temperature. Pure ferrite has a Brinell hardness of about 80.

The properties of pearlite are evidently those of eutectoid steel in its normal, i.e. pearlitic, condition, from which we may infer that pearlite has a tenacity of some 115,000 pounds per square inch, an elongation of some 10 per cent, a Brinell hardness of about 200, and for reasons later to be explained, that it possesses maximum hardening power.

With the exception of its very great hardness (Brinell hardness 600+) little is positively known as to the physical properties of cementite. Its tensile strength probably does not exceed 5000 pounds per square inch, and may be considerably less, while its ductility must be practically nil. It possesses no hardening power.

These properties of the constituents of steel in its normal condition are tabulated below:

Constituents	Tensile Strength lbs. per sq. in.	Elongation % in 2 in.	Hardness Brinell	Hardening Power
Ferrite	40,000±	50±	80±	None
Pearlite	115,000±	10±	200±	Maximum
Cementite	5,000(?)	0	600+	None

Tenacity of Steel vs. Its Structural Composition. — Knowing the physical properties of the three constituents of pearlitic steel, it should be possible to foretell with some degree of accuracy the physical properties of any steel of known structural composition, on the reasonable assumption that these constituents impart to the steel their own physical properties in a degree proportional to the amounts in which they are present. The properties of steel made up for instance of 50 per cent ferrite and 50 per cent pearlite should be the means of the properties of ferrite and of pearlite. Let us assume such reasoning to be correct and let us apply it to the tensile strength first of hypo-eutectoid steel and then of hyper-eutectoid steel.

The tensile strength (T) of any hypo-eutectoid steel will be expressed by the

following formula in terms of its structural composition, that is in terms of the percentages of ferrite (F) and pearlite (P) which it contains:

$$T = \frac{40{,}000\ F + 115{,}000\ P}{100}$$

in which 40,000 represents the tensile strength of ferrite, and 115,000 the strength of pearlite.

Or, simplifying:

$$T = 400\ F + 1150\ P$$

or again in terms of pearlite alone, since $F = 100 - P$

$$T = 400\ (100 - P) + 1150\ P$$

or $$T = 40{,}000 + 750\ P$$

or finally in terms of carbon, since $P = 117\ C$

$$T = 40{,}000 + 87{,}750\ C$$

Steel containing 0.50 per cent carbon should have a tensile strength, *when in a pearlitic condition*, of 83,875 pounds per square inch.

The values obtained for various hypo-eutectoid steels should be accurate only for steel in what has been termed in these chapters its normal condition, that is steel which has been worked, reheated to a high temperature, and slowly cooled. It should be noted, however, as later explained, that steel worked and finished at a fairly high temperature is practically in this so-called normal condition, so that the formula may be used, and fair results expected, to calculate the tensile strength of such hot worked steel in *a direction parallel to the forging or rolling*. If the steel be worked until its temperature is quite low and, especially, if it be cold worked, it is well known that its tensile strength is generally increased. Neither can the formula be used, of course, in the case of hardened steel or of steel castings. It may, however, be applied to steel castings which have been properly annealed, when the tensile strength may be brought up to the level of steel forgings finished fairly hot, as explained in another chapter.

Again the formula is of value only in case of commercial steels containing the usual proportions of impurities, especially of manganese. It applies only to steels in which the percentage of manganese varies roughly with the carbon content from some 0.20 to 0.80 per cent. The presence of a larger proportion of manganese would increase the tenacity materially.

Passing to the tensile strength of hyper-eutectoid steel, our ignorance as to the tenacity of cementite does not permit the writing of a formula with the same degree of confidence. Let us assume, tentatively, however, that cementite has a tensile strength of 5000 pounds per square inch and then proceed as we did in the case of hypo-eutectoid steel.

The tensile strength of any hyper-eutectoid steel may be expressed by the following formula in terms of the percentages of pearlite (P) and cementite (Cm) which it contains:

$$T = \frac{115{,}000\ P + 5000\ Cm}{100}$$

or, simplifying:

$$T = 1150\ P + 50\ Cm$$

or in terms of pearlite only, since Cm = 100 − P

$$T = 1150\ P + 50\ (100 - P)$$
$$T = 5000 + 1000\ P$$

or since, as previously shown, P = 115 − 17 C

$$T = 5000 + 1100\ (115 - 17\ C$$

or, simplifying:

$$T = 131{,}500 - 18{,}700\ C$$

Pearlitic steel containing 1 per cent carbon should have a tensile strength of 112,800 pounds per square inch.

Steel of Maximum Strength. — From the preceding considerations it seems evident that eutectoid steel must possess maximum tensile strength since the influence of the presence of ever so small an amount of free ferrite in hypo-eutectoid steel or of free cementite in hyper-eutectoid steel must necessarily be a weakening one, because of the relative weakness of free ferrite and free cementite as compared to the strength of pearlite. By most writers, on the other hand, steel of maximum tenacity is often stated to contain in the vicinity of 1 per cent carbon, that is to be slightly hyper-eutectoid.

It is not clear, however, that the results upon which the statement is based were obtained in testing steel in its *pearlitic condition.* On the contrary it seems probable that a large number of the steels tested were in a sorbitic rather than in a pearlitic condition because of relatively quick cooling through the critical range, as explained in a subsequent chapter. And while it appears that pearlitic steel must have its maximum tenacity when composed entirely of pearlite, it may well be that when in a sorbitic condition maximum strength corresponds to a higher degree of carburization, i.e. 1 per cent, because sorbite may contain and indeed often does contain more carbon than pearlite. Indeed the cases on record show that when the steels were made pearlitic through very slow cooling, maximum tenacity corresponds closely to the eutectoid composition. Arnold, for instance, tested a series of very pure carbon steels and after slow cooling in the furnace from 1000 deg. C. he found a very sharp maximum in the tenacity corresponding to 0.89 per cent carbon. On cooling these same steels in air, on the contrary, and therefore making them sorbitic, maximum tenacity corresponded to 1.20 per cent carbon.

J. H. Nead reports the maximum strength of annealed, and therefore pearlitic, steel to be 114,000 pounds per square inch, and to correspond to 0.83 per cent carbon. In heat treated (sorbitic?) steel, he finds the maximum strength at 1.20 per cent carbon.

Ductility of Steel vs. Its Structural Composition. — From the known ductility, as expressed by its elongation under tension, of ferrite and the known elongation of pearlite, respectively 50 and 10 per cent in two inches, it should be possible to work out a formula expressing the ductility of any hypo-eutectoid steel in the annealed (pearlitic) condition.

In terms of ferrite and pearlite the ductility should be

$$D = \frac{50\ F + 10\ P}{100}$$

or, simplifying:

$$D = .5\ F + .1\ P$$

or, in terms of pearlite alone, since F = 100 − P

$$D = .5\ (100 - P) + .1\ P = P$$

and since P = 117 C, the ductility in terms of carbon will be:

$$D = 50 - 46.8\ C.$$

Pearlitic steels for instance containing 0.25 and 0.50 per cent carbon should have elongations respectively of 38.3 and 26.6 per cent in two inches.

Brinell Hardness. — The Brinell hardness of steel when in its *pearlitic condition* may be represented by the formula

$$H = a + bx$$

in which a represents the hardness of carbonless iron, b a constant, and x the percentage of carbon in the steel.

Assuming the Brinell hardness of ferrite to be 80, we have

$$H = 80 + bx$$

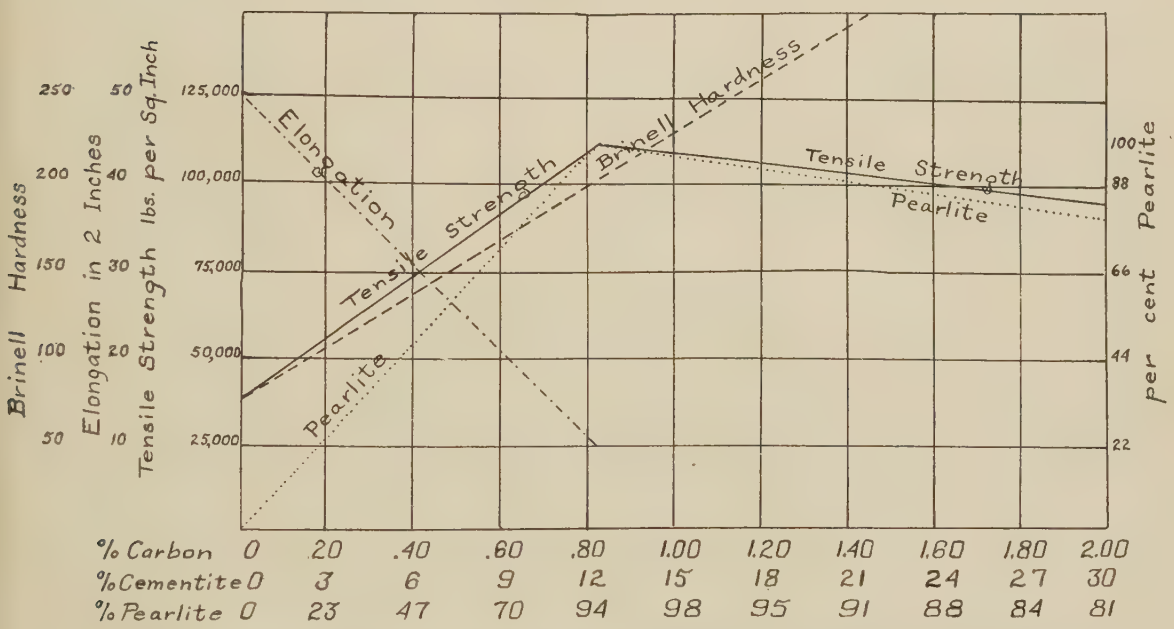


Fig. 67. Diagram showing the relations between the tenacity, hardness, and ductility of steel and its carbon content.

Assuming further the Brinell hardness of eutectoid steel (C = 0.85 per cent) to be 200, then we have the following equation:

$$200 = 80 + b \times 0.85$$

or

$$b = \frac{200 - 80}{0.85} = 141$$

hence

$$H = 80 + 141\ x$$

should give us the Brinell hardness of any carbon steel in a pearlitic condition. Steels containing respectively 0.25, 0.50, and 0.75 per cent carbon should have, when pearlitic, Brinell hardness of 115, 155, and 185. Or knowing the Brinell hardness, H, of the steel in its *pearlitic condition*, its carbon content, x, should be approximately.

$$x = \frac{H - 80}{141}$$

Diagram Showing the Relation between the Tenacity Hardness and Ductility of Steel and Its Carbon Content. — By plotting the formulas suggested in this chapter to express the relation between the carbon content of steel and its tenacity hardness and ductility the curves of Figure 67 are obtained. A fourth curve has been added showing the variation of the amount of pearlite with the carbon content.

Neumann Bands in Hypo-Eutectoid Steel. — When steel containing free ferrite is subjected to impact or dynamic stresses, the ferrite grains are frequently found to contain Neumann bands (Fig. 68). They result from sudden deformation. If the blow or shock has caused fracture, the more sudden that fracture the more localized generally in the vicinity of the fracture will be the deformation, hence likewise the Neumann bands; they are not found at any appreciable distance from the fracture. A rupture so sharp and so sudden as to imply complete absence of deformation in the vicinity of the fracture should not be accompanied by Neumann bands.

Neumann bands have never been observed in pearlite, cementite, or other constituent of steel, hence they do not occur in eutectoid or hyper-eutectoid steel, nor in martensitic, troostitic, or sorbitic steel.

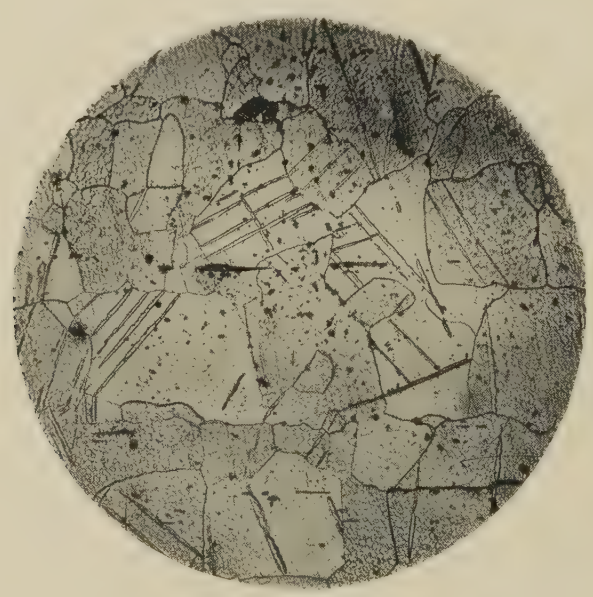


Fig. 68. — Neumann bands in ferrite. (F. B. Foley.)

CHAPTER VI

IMPURITIES IN STEEL

Metallic Impurities. — Commercial grades of steel always contain, besides carbon, varying amounts of silicon, phosphorus, sulphur, and manganese, often an appreciable proportion of copper, and traces at least of many other metals and metalloids. These may be called the metallic impurities. Sulphur, however, is sometimes classified as a non-metallic impurity, as later explained.

Non-Metallic or Oxidized Impurities. — Non-metallic or oxidized impurities, chiefly oxides, sulphides, and silicates of iron and manganese, are also frequently found in steel, principally through the retention by the metal of some of the slag produced during the refining operation, of some detached particles of refractory materials, and of some products resulting from the addition of recarburizers. They are known as "enclosures" or "inclusions."

Metallic vs. Non-Metallic Impurities. — There is a sharp distinction between the behavior of metallic and non-metallic impurities, the former, with the exception of sulphur, forming true alloys with the contaminated metal, the latter occurring as inclusions, their association with the metal being purely mechanical.

Gaseous Impurities. — Steel always contain some gases, apparently held in solution and called "occluded" gases, chiefly hydrogen, nitrogen, and carbon monoxide (CO), as well as oxygen probably present as FeO.

Occurrence of Impurities. — Like those occurring in metals in general (Chapter II), the impurities present in iron and steel may remain uncombined, as for instance graphite, or they may form a chemical combination (*a*) with iron (Fe_3C, FeSi, Fe_3P, FeS, FeO) or (*b*) with another impurity (MnS and Mn_3C). The uncombined impurity or the chemical compound may then (*a*) be present as inclusions (graphite, MnS, FeS, SiO_2, MnO, FeO), (*b*) form one of the constituents of a eutectic (Fe_3P) or of a eutectoid (Fe_3C) or (*c*) form a solid solution with iron (Fe_3C, FeSi, Fe_3P) according to heat treatment and other conditions, as later explained.

Impurities vs. Physical Properties of Steel. — It is well known that surprisingly small proportions of some of the metallic impurities just mentioned may have a very marked influence upon the physical properties of steel. Some 0.2 per cent phosphorus, for instance, renders many grades of steel so brittle as to unfit them for most commercial uses, while some .15 per cent of sulphur or of oxygen may make it hopelessly red-short. And as it is logical to suppose that there exists a very close relation between the structure of a metal and its physical characteristics, we naturally expect to find important structural changes corresponding to such marked alterations of physical properties. We should expect, for instance, the structure of a high phosphorus, brittle steel to be quite different from the structure of a low phosphorus, tough steel of otherwise identical composition. In the present state of metallography

the microscope does not always reveal such differences of structures as we are led to look for. We may reasonably anticipate, however, that, as the science progresses, structural differences will be detected of a magnitude fairly in keeping with the deep changes of physical properties brought about by slight changes of chemical composition. Indeed in recent years material advance has been made in this direction, and the influence of the usual impurities upon the properties of steel has been on the whole satisfactorily accounted for by metallographic methods, as will be apparent from the description which follows.

Silicon in Steel. — All grades of steel contain a trace at least of silicon (Si) and occasionally as much as 0.5 per cent, and even more, most grades containing between 0.05 and 0.3 per cent.

When present in such small proportion silicon is entirely dissolved in the iron, with which it forms a solid solution.[1] It is probable, however, that it is not held in solution by the iron in its elementary condition, Si, but rather as a silicide of iron, FeSi.[2] Assuming the atomic weight of iron to be exactly 56 and that of silicon 28 it will be evident that 28 parts by weight of silicon produces 56 + 28 or 84 parts by weight of FeSi, or that silicon produces exactly 3 times its own weight of FeSi (84 : 28 = 3). For instance 0.1 per cent silicon in the steel will give rise to the formation of 0.3 per cent of FeSi, and this small amount of iron silicide will be held in solid solution by the iron. The ferrite of commercial steel, therefore, always contains a small amount of silicon in the form of an iron silicide, and this applies to the ferrite forming part of the pearlite of all slowly cooled steels as well as to the free ferrite of hypo-eutectoid steel.

It has been stated in another chapter that when an impurity forms a solid solution with the contaminated metal, changes of crystalline forms are not generally observed. This is true in the present case, for there is apparently no structural difference between a steel with some 0.3 or 0.4 per cent silicon and a steel nearly free from that element but otherwise of identical composition. The presence of silicon in steel cannot as yet be satisfactorily detected, even qualitatively, by metallographic methods, although we have the unquestionably accurate statement of Le Chatelier that silicon causes ferrite to etch more slowly.

In view of the similarity of structure between steel containing much silicon (i.e. several tenths of 1 per cent) and steel practically free from it, we should expect that the presence of a small amount of silicon cannot affect materially the properties of steel, and this we know to be the case. It is universally known that silicon improves the soundness of ingots and other castings by opposing the formation of blowholes. This is generally ascribed to its causing the blowhole-forming gases — hydrogen, nitrogen, etc. — to be retained in solid solution during solidification. It promotes the deoxidation of the molten steel through the formation of silicon dioxide, SiO_2, hence again the soundness of the castings.

Phosphorus in Steel. — Steel of satisfactory quality contains from a trace to 0.1 per cent of phosphorus (P). As in the case of silicon this small amount of phosphorus

[1] Some writers believe, apparently on good ground, that in cast iron at least, a metal which generally contains a considerable amount of silicon, a portion of that element crystallizes with the cementite, decreasing its stability, as later explained. In steel, however, the proportion of silicon present is small, and if any of it dissolves in the cementite it must be in so small a quantity as to be negligible.

[2] Some writers mention $FeSi_2$ as the formula of the iron silicide present in steel but this contention is not well supported by experimental evidences.

is held in solid solution by the iron, not, however, in the elementary state, P, but as the phosphide of iron, Fe_3P. The atomic weight of iron being 56, that of phosphorus 31, and the phosphide containing three atoms of iron for each atom of phosphorus, it will be obvious that 31 parts by weight of phosphorus will form $3 \times 56 + 31$ or 199 parts of the phosphide Fe_3P, or roughly, 1 part by weight of phosphorus will give rise to the formation of 6 parts of phosphide. For instance, the presence in steel of 0.05 per cent phosphorus results in the formation of 0.3 per cent of Fe_3P held in solid solution by the ferrite, this being true of the ferrite included in the pearlite of all slowly cooled steel as well as of the free ferrite of hypo-eutectoid steel.

While phosphorus in common with other metallic impurities forming solid solutions does not alter the crystalline form of steel, it is believed by some to have a marked tendency to enlarge the grains of the metal, which tendency would account, in part at least, for the well-known brittleness imparted to steel by phosphorus when present in excess of 0.1 per cent. The brittleness caused by a large grain will be considered further in another chapter.

Except for this possible enlargement of the grains, microscopical examination does not reveal the presence of the usually small percentages of phosphorus occurring in steel, unless it be segregated, although it is said by some writers that phosphorus as well as manganese causes ferrite to etch darker. The existence of portions richer in phosphorus than others may be detected by means of Stead's and other similar reagents. Phosphorus has a marked tendency to segregate in the upper part of ingots and other castings, as well as in the portions of dendrites last in solidifying. We may call the former "major" segregation, and the latter "dendritic" segregation. These phenomena will be further dealt with in another chapter.

The diffusion of phosphorus takes place very slowly even at high temperature, from which it follows that even long annealing fails to remove completely the dendritic segregation of that element. It has been shown by Stead that phosphorus expels the carbon from portions of the steel in which the former is present, from which it follows that phosphorus-rich portions generally contain little carbon (see ghost lines). Causing the carbon to diffuse into the phosphorus-rich areas by heating above the critical range, if it is followed by slow cooling, results in the carbon being again expelled from these areas in passing through the critical range.

As much as 0.1 per cent phosphorus is considered desirable in sheet bar steels in order to prevent the sheets from sticking together during the rolling. Phosphorus is sometimes purposely added to some steels to improve cutting properties. Phosphorus increases slightly the hardness and strength of steel and decreases its ductility. The electrical resistance is slightly increased.

Sulphur in Steel. — Steel of satisfactory commercial quality may contain from a mere trace to some 0.1 per cent sulphur, generally between 0.01 and 0.05 per cent. It is well known that manganese and sulphur have very great reciprocal affinity so that when brought together at a high temperature they combine chemically to form the sulphide of manganese, MnS. This is what happens in steel which always contains manganese as well as sulphur. From the atomic weight of manganese, 55, and that of sulphur, 32, it will be seen that 32 parts by weight of sulphur produces 87 parts of MnS, or approximately $2\frac{1}{2}$ parts of sulphide for each part of sulphur. Steel with 0.05 per cent sulphur, for instance, will contain about 0.125 per cent of MnS, provided, of course, there is enough manganese present to satisfy the sulphur, which must necessarily be so in properly made steel.

The existence of the sulphide of manganese, MnS, in steel has been conclusively proven. In steel castings it occurs as rounded areas the color of which is generally described as pale or dove gray or slate color. In forgings it occurs in elongated particles, bands, or strings of the same tint, running parallel to the direction of the forging or rolling (Figs. 69 and 70).

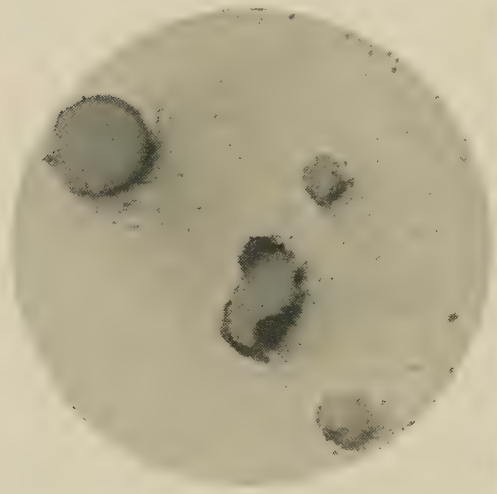


Fig. 69. — Manganese sulphide in steel casting. Magnified 640 diameters. (Boylston.)

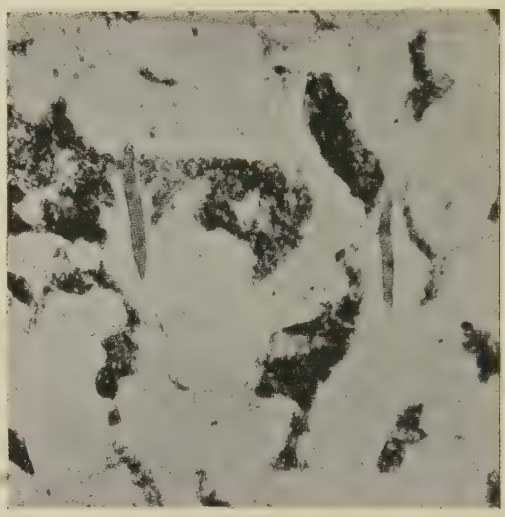


Fig. 70. — Steel. Forged. Hypo-eutectoid. Manganese sulphide in ferrite areas. Magnified 300 diameters. (Levy.)

According to Le Chatelier, MnS has a melting point superior even to that of iron, solidifying, therefore, first, and the bulk of it rising to the top of the bath or ingot, manganese being in this way helpful in removing sulphur from steel. Some writers, however, question this higher melting point of MnS. Levy reports that the melting point of pure MnS is probably not far from 1400 deg. C. and, therefore, below the melting point of hypo-eutectoid steel at least, while the presence of some FeS would lower materially its melting point. It appears probable that the solidification of the sulphide globules must follow and not precede that of the iron.

This view seems to be supported by the location of the sulphide particles at the boundaries of the pearlite grains of eutectoid steel, in the free ferrite of hypo-eutectoid steel or in the free cementite of hyper-eutectoid steel. What MnS is retained by the solid steel, since it occurs as shown in the shape of small individual grains or elongated particles, can only injure the metal through breaking up its continuity and, in view of the very small amount of sulphur and, therefore, of MnS, present in steel of good quality, it is evident that this breaking up and its action upon the properties must be very slight. This is in agreement with the known fact that a small amount of sulphur in steel containing also the proper amount of manganese has no appreciably injurious effect. Portevin believes that sulphur tends to make steel forgings brittle, when tested in a transverse direction.

So-called "free-cutting" or "screw stock" steel, intentionally high in sulphur (0.1 — 0.2 per cent S), is manufactured because of improved cutting properties, small chips being obtained instead of long turnings.

It is generally believed that manganese sulphide decreases the resistance of iron and steel to corrosion.

In case sulphur occurs in excess over the amount needed to form the sulphide MnS with the manganese present in the steel, the excess sulphur, that is the sulphur left over after satisfying the manganese, combines with some of the iron, forming the iron sulphide FeS. It should be noted at once, however, that it requires less than 2 parts by weight of manganese (atomic weight 55) to combine with 1 part of sulphur (atomic weight 32). In other words if the steel contains twice as much manganese as it does sulphur, this should theoretically be enough to convert the whole of the sulphur into the sulphide MnS. Stead writes, however, that steel should contain at least eight times as much manganese as sulphur. As it is very seldom indeed that

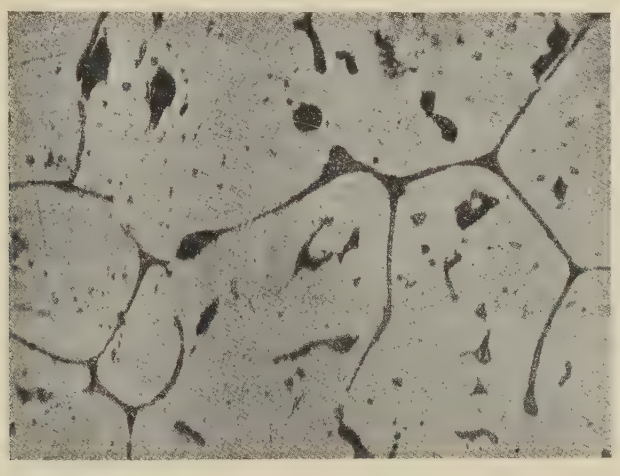


Fig. 71. — Red-short steel. Magnified 300 diameters. Sulphur 0.54 per cent. Unetched. Network of FeS. (Ziegler.)

steel does not contain a sufficient proportion of manganese, the occurrence of free FeS in steel should be very rare. According to Levy, however, MnS and FeS are readily soluble in each other in the solid state, MnS being capable of holding as much as 50 per cent of FeS in solid solution. This writer claims that MnS is seldom free from FeS, even when the steel contains considerable manganese, the mass action exerted by the presence of so large a proportion of iron preventing the manganese from taking hold of the totality of the sulphur, in spite of its greater affinity for it. MnS nearly free from FeS has a clear dove or gray color, free from yellowish tints, while its color becomes more yellowish as the proportion of FeS increases. Levy notes also that in high carbon steel the MnS areas are generally colored darker than in low carbon steel, indicating greater freedom from FeS, apparently owing to the fact that in high carbon steel the mass action exerted by iron is not so great, since it contains less iron. McCance, however, does not believe that MnS inclusions ever contain FeS.

The sulphide FeS exhibits a marked tendency to form continuous envelopes or membranes surrounding each grain of pearlite (Fig. 71) and probably consisting of a eutectic alloy of iron and iron sulphide (the composition of the eutectic is apparently FeS 85 per cent, Fe 15 per cent). These membranes being weak and brittle, impart

weakness and brittleness to the steel. The well-known red-shortness caused by sulphur in the absence of a sufficient amount of manganese (to form MnS) is probably due to the low melting point (950 deg. C. according to some writers) of this iron-iron sulphide eutectic. At a high temperature the melting of this eutectic destroys the cohesion between the grains of the metal, resulting in cracks being developed during the process of forging or rolling, and in extreme cases in the metal actually breaking into several pieces. The presence of a large amount of FeS in some Bessemer steel at the end of the blow, before the addition of manganese, is undoubtedly largely responsible for the marked red-shortness of the metal at this stage of the operation. In the complete absence of manganese the presence of 0.02 per cent sulphur suffices to produce red-shortness.

Under the microscope FeS appears yellow or pale brown.

The following is quoted from Stead: "The researches of Rohl have demonstrated beyond doubt that ferrous and manganese sulphides crystallize together in the proportions of 60 per cent FeS and 40 per cent MnS = $Fe_3Mn_2S_5$ and in mixtures containing increasing quantities of manganese sulphide up to 100 per cent, forming homogeneous isomorphous compounds of $Fe_3Mn_2S_5$, all of which under the microscope have the same appearance. Levy and Law, however, state that the homogeneous substance which contains the most FeS is lighter in color than that containing less.

"When the FeS exceeds 60 per cent in the mixture a eutectic consisting of 7 per cent MnS and 93 per cent FeS appears, having a freezing point of 1181 deg. C.

"When iron in excess is present in addition to an excess of FeS over the mixture $Fe_3Mn_2S_5$, a ternary eutectic is formed, freezing at 980 deg. Rohl found the freezing point of pure MnS to be 1620 deg., or about 120 deg. higher than that of pure iron, and the freezing point of the compound $Fe_3Mn_2S_5$, 1365 deg.

"Judging from these most valuable researches, it may be accepted beyond any doubt that when iron sulphide, and what appears to be manganese sulphide, are found associated together in the same sulphide inclusions, what looks like MnS is not that compound but is $Fe_3Mn_2S_5$."

It has been contended by some that a portion of the sulphur present in steel and cast iron is dissolved in the cementite and that its presence increases the stability of that constituent. It seems probable, however, in view of the very small amount of sulphur generally present in steel and of the relatively large amount of manganese, that this possible contamination of cementite by sulphur, if it occurs at all, may be neglected. This has been done in the present chapter, it having been assumed that the totality of the sulphur is present as MnS or as MnS and FeS in the form of mechanical inclusions.

Sulphur Printing. — As explained in Appendix I the presence of sulphur in steel and iron, especially when segregated, may sometimes be detected by the taking of so-called "sulphur prints."

Manganese in Steel. — It has been seen that manganese combines readily with sulphur and that the resulting manganese sulphide, MnS, either alone or combined with some FeS, can be detected in polished steel sections as a pale or dove gray constituent assuming the shape of rounded areas in castings and of bands or threads in forgings. Manganese silicate is also occasionally found in steel, as later explained, and may sometimes be mistaken for MnS. Satisfactory tests for the distinction of these two constituents will be described.

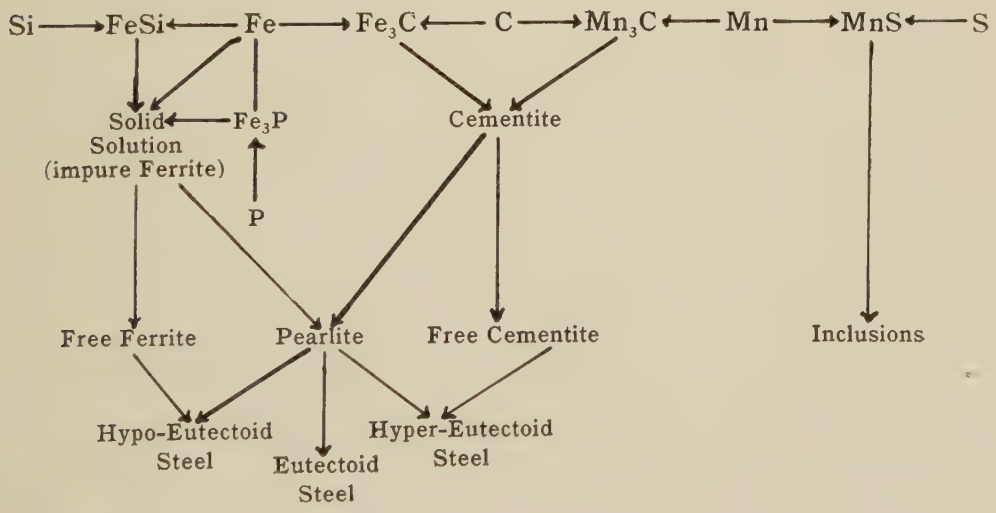
When manganese occurs in excess over the amount required to form MnS with the totality of the sulphur present, as is almost universally the case, the manganese in excess combines with some of the carbon to form the carbide of manganese, Mn_3C, and this carbide is found associated with the iron carbide, Fe_3C, in cementite. The

cementite of commercial steel, therefore, is seldom a pure iron carbide, containing on the contrary varying amounts of Mn_3C. Since iron and manganese have practically the same atomic weight, however (55 and 56 respectively), it remains practically true that carbon forms 15 times its own weight of cementite, even when the latter contains a large proportion of Mn_3C.

There is no metallographic test by which cementite free from manganese can be distinguished from cementite rich in Mn_3C.

Some authors mention the possible presence of the manganese silicide, MnSi, in steel, while solid solutions between manganese and iron are frequently referred to. While manganese and iron (ferrite) undoubtedly form solid solutions, it does not seem likely that these are produced when manganese is present in small proportion, say not over 1 per cent. In that case it seems more probable that manganese is found in the two forms described above, (1) as a manganese sulphide MnS, containing practically the totality of the sulphur in steel of good quality, that is containing not over 0.05 per cent sulphur and not less than 0.25 per cent manganese, and (2) as the manganese carbide Mn_3C, associated with Fe_3C in cementite. It is universally known that manganese promotes the soundness of steel castings through its deoxidizing action on the liquid steel, and that it promotes forgeability through the formation of harmless manganese sulphide instead of iron sulphide, the latter being a source of red-shortness.

Decreasing somewhat the carbon content, and increasing the manganese to 1 or 1.5 per cent, increases the tenacity and elastic limit with but slight decrease of ductility. Some believe that resistance to shock, as ascertained by the Charpy test, is likewise increased. According to Hoyt, manganese by retarding the rate of coalescence or grain growth renders steel less sensitive to the effect of high rolling temperature, while it also promotes plasticity. It increases, however, the tendency to crack on quenching.



The behavior of metallic impurities in iron is shown diagrammatically in the above table, in which it is clearly indicated that (1) silicon combines with iron to form FeSi; (2) carbon combines with iron to form Fe_3C, and with manganese to form Mn_3C;

(3) maganese combines with iron as stated, and with sulphur to form MnS; (4) sulphur combines with iron as stated; (5) phosphorus forms Fe_3P with iron; (6) FeSi and Fe_3P dissolve in iron to form impure ferrite; (7) Fe_3C and Mn_3C form cementite; (8) impure ferrite and cementite form pearlite; (9) free ferrite and pearlite make up hypo-eutectoid steel; (10) free cementite and pearlite make up hyper-eutectoid steel; (11) MnS is present as inclusions.

Chemical vs. Structural Composition. — Knowing the probable chemical forms of the five metallic impurities always present in steel, carbon, silicon, phosphorus, sulphur, and manganese, as well as their structural associations, it will be interesting and profitable to consider accordingly the proximate chemical composition as well as the ultimate and proximate structural compositions of a steel of known ultimate chemical composition. Let us assume a steel of the following ultimate chemical composition:

C	0.50 per cent
Mn	0.80 " "
S	0.05 " "
P	0.04 " "
Si	0.10 " "
Fe (by diff.)	98.51 " "
	100.00 " "

Bearing in mind the atomic weights of these elements (Fe, 56; C, 12; Mn, 55; S, 32; P, 31; Si, 28) and the formulas of the chemical compounds formed (MnS, FeSi, Fe_3P, Mn_3C, Fe_3C), it will be readily seen that:

(1) 0.05 per cent S will give rise to the formation of 0.13 per cent MnS.
(2) 0.13 per cent MnS contains about 0.08 per cent Mn.
(3) This leaves $0.80 - 0.08 = 0.72$ per cent manganese in excess to combine with C.
(4) 0.72 per cent Mn will form 0.77 per cent Mn_3C.
(5) 0.77 per cent Mn_3C contains about 0.05 per cent carbon.
(6) This leaves $0.50 - 0.05 = 0.45$ carbon to combine with iron.
(7) 0.45 per cent carbon results in the formation of 6.75 per cent of Fe_3C.
(8) 0.04 per cent of P corresponds to about 0.25 per cent of Fe_3P.
(9) 0.10 per cent Si gives 0.30 per cent FeSi.

The proximate chemical composition of the steel considered will be

Fe_3C	6.75 per cent
Mn_3C	0.77 " "
Fe_3P	0.25 " "
FeSi	0.30 " "
MnS	0.13 " "
Fe (by diff.)	91.80 " "
	100.00 " "

As to the ultimate structural composition of the steel, we know that the cementite contains the Fe_3C and the Mn_3C, hence we have $6.75 + 0.77 = 7.52$ per cent cementite. In pure steel the percentage of cementite would have been $0.50 \times 15 = 7.50$ per cent. The slight difference between the two numbers is due to the presence of manganese in the commercial steel, and to a slight difference between the atomic weights of man-

ganese and that of iron (55 compared to 56), a difference so small that for all practical purposes we may assume that in commercial steels as well as in pure steel the percentage of carbon multiplied by 15 gives the amount of cementite formed. The total ferrite present in this steel contains all the free iron, as well as the small proportions of Fe_3P and FeSi present, hence this steel contains 91.80 + 0.25 + 0.30 = 92.35 per cent total ferrite. In pure steel the proportion of total ferrite would have been 100 − 7.50 or 92.50 per cent. The difference between the two values is evidently due to the presence of a trifle greater amount of cementite, and to the presence of 0.13 per cent MnS.

The ultimate structural composition of the steel under consideration is, therefore:

Total ferrite	92.35	per cent
Cementite	7.52	" "
MnS	0.13	" "
	100.00	" "

Finally its proximate structural composition will be, since the pearlite of hypoeutectoid steel contains 7.8 times the weight of total cementite:

Pearlite	7.52 × 7.8 = 58.66	per cent
Free ferrite (by diff.)	41.21	" "
MnS	.13	" "
	100.00	" "

Ignoring the presence of impurities, the quick method described in Chapter V would have given pearlite 58.50 per cent, ferrite 41.50 per cent, i.e. values which may be considered identical for any practical purposes. It follows from this that in calculating the structural composition of any carbon steel of ordinary commercial quality the presence of the impurities need not be considered; the steel may be treated as if it were made exclusively of iron and carbon.

The relation between chemical and structural compositions, both ultimate and proximate, is further shown in the following table:

CHEMICAL COMPOSITION				STRUCTURAL COMPOSITION			
Ultimate		Proximate		Ultimate		Proximate	
	%		%		%		%
Fe(by diff.)	98.51	Fe(by diff.)	91.80	Total Ferrite	92.35	Free Ferrite	41.21
Si	0.10	FeSi	0.30			Pearlite-Ferrite	51.14
P	0.04	Fe_3P	0.25				
C	0.50	Fe_3C	6.75	Cementite	7.52		58.66 Pearlite
Mn	0.80	Mn_3C	0.77				
S	0.05	MnS	0.13	MnS	0.13		0.13
	100.00		100.00		100.00		100.00

Non-Metallic or Oxidized Impurities. — As already mentioned, steel generally contains varying amounts of non-metallic, oxidized impurities frequently called "enclosures," or "inclusions," while Hibbard proposed for them the name of "sonim," in which "so" stands for solid, "n" for non-metallic, and "im" for impurities. These impurities are derived mainly (1) from the retention by the metal of minute particles

of the slag formed during the process of manufacture, (2) from small pieces of refractory materials detached from the linings of furnaces and ladles, and (3) from the reaction-products resulting from the introduction of recarburizers or other additions.

According to Hibbard the formation of inclusions is due almost entirely to the "washing" action of the additions, principally of manganese, in combining with the dissolved oxides, sulphides, and silicates which are present in the steel at the end of the melting process before the manganese is added, since inclusions rich in manganese must necessarily have formed after the addition of that constituent. Stead, on the other hand, expresses the belief that the silicates, at all events, are due to oxidation of manganese and silicon occurring during the passage of the molten steel through the air in passing from the ladle into the molds. In the case of iron oxide it seems probable that minute particles of it remain in suspension in the molten steel, forming as many minute inclusions after solidification, while another portion, dissolved in the liquid metal, is in part precipitated during solidification.

In Rosenhain's opinion it is not proven that the sulphides and silicates are not soluble in molten steel.

After solidification the association between the inclusions and the steel remains a purely mechanical one; they commonly occur as rounded or elongated particles embedded in the metal. The slag formed during the process of manufacture, some of which may be retained by the steel, consists essentially of silicates of iron and manganese, the refractory material from linings of silica and alumina, and the inclusions resulting from recarburizing or other additions of MnS, MnO, Al_2O_3, and SiO_2 from the following reactions, as indicated by Hoyt:

$$\begin{aligned} FeS + Mn &= MnS + Fe \\ FeO + Mn &= MnO + Fe \\ 3\,FeO + 2\,Al &= Al_2O_3 + 3\,Fe \\ 2\,FeO + S &= SO_2 + 2\,Fe \end{aligned}$$

Some iron oxide may also be present in case of incomplete deoxidation of the bath.

Some of these inclusions are plastic, being drawn out in forging or rolling, notably the silicates and manganese sulphide, while others, such as the oxides, are non-plastic. It is claimed by Comstock, apparently on good ground, that while inclusions of Al_2O_3 are not themselves elongated, they form elongated clusters in the direction of the work.

While inclusions drawn out in forging may not affect appreciably the properties of the steel when tested in a longitudinal direction, they may affect it deeply in a transverse direction when they decrease the strength, ductility, and impact toughness.

MnS can generally be readily distinguished from other inclusions because of its characteristic dove gray color, its globular shape in castings (Fig. 69), and, owing to its placticity, the ease with which it is elongated in forgings (Fig. 70). It seems reasonable to assume that the paler its color the greater its purity, and that a yellowish tint points to the presence of some FeS. Pure FeS, a very rare constituent of steel, has a decidedly yellow color and is more brittle. MnS generally occurs in the free ferrite of hypo-eutectoid steel, between the pearlite grains of eutectoid steel, or in the free cementite of hyper-eutectoid steel.

Silicates are decidedly darker than MnS (Figs. 72 and 73), affording a means of distinguishing between them even when they are associated in the same particles, as it sometimes happens (Fig. 72). Silicates because of their relative brittleness are

frequently broken and torn by the forging operation (Fig. 73). Sometimes the manganese sulphide forms dendrites embedded in a silicate matrix.

Stead recommends the placing of a drop of sulphuric acid on the polished speci-

Fig. 72. — Manganese sulphide (light constituent) and manganese silicate in steel. Magnified 1000 diameters. (Law.)

Fig. 73. — Manganese sulphide (light constituent) and iron silicate in mild steel. Unetched. Magnified 1000 diameters. (Law.)

men, when H_2S gas will be evolved where MnS is present, particles of silicates of manganese, on the contrary, evolving no gas. The dissolving of MnS also leaves pits. Stead further advises heat tinting as the best means of distinguishing between the sulphide and the silicate, the heating to be continued until the specimen has assumed

a light brown coloration, when the MnS remaining bright can be sharply differentiated from the silicate.

No very satisfactory metallographic tests have so far been found to distinguish between oxides and silicates or between iron silicate and manganese silicate. Matweieff's attempts in that direction have been described in Chapter IV.

They are summed up by Rosenhain as follows: "According to their behavior under these reagents (hydrogen and superheated steam), the enclosures may be divided into three groups or classes:

"A. Stable bodies which are not acted upon either by hydrogen at 300° C., by superheated steam, or by weak organic acids. These are the silicates of iron and manganese.

"B. Bodies which are reduced to the metallic state by the action of hydrogen at 300° C. and are acted upon by steam but are unaffected by weak organic acids. These are the oxides of iron and manganese. Oxide of manganese is not reduced by hydrogen when by itself, but in the presence of iron oxide reduction of both metals takes place. On re-polishing a sample after heating in hydrogen, the regions previously occupied by oxides appear as bright metal, like the ferrite of the surrounding iron or steel, but the presence of manganese may be detected by etching with a very dilute alcoholic solution of ferric chloride. Iron free from manganese is only very slightly colored, but if manganese is present, the reagent produces rapid coloration.

"C. Not affected by hydrogen or steam, but attacked by weak organic acids (such as tartaric acid). These are the sulphides of iron and manganese; the former is rapidly colored by this acid, while sulphide of manganese is only slowly attacked. The behavior of the sulphides, which are mixtures or solid solutions of the iron and manganese sulphides, is not considered by Matweieff, but in the light of the work of Levy these mixed sulphides require particular study from this point of view."

Rosenhain rightly adds that the use of gaseous reagents at moderately high temperatures is a somewhat cumbrous manipulation, particularly because, if general tarnishing of the polished specimens is to be avoided, the hydrogen must be specially purified. It is to be hoped, therefore, that future research may yet find simpler means of identifying these substances.

At the end of the refining operation by which steel is produced, especially towards the latter part of the Bessemer blow, a considerable amount of iron oxide is formed and in spite of the steps taken for removing it from the bath (addition of manganese, etc.) some of it, occasionally quite a little, is retained by the metal, when it is a source of red-shortness, besides having other detrimental effects. This iron oxide generally occurs as small rounded particles visible in the polished section before etching.

Comstock indicates, as a means of distinguishing between sulphides and oxides, etching with boiling sodium picrate for ten minutes, by which the sulphide inclusions are blackened, while oxide inclusions remain unaffected, thus making it possible to differentiate between manganese sulphide and iron oxide inclusions, both of which are light gray. It is sometimes advisable, when it is desired to ascertain the presence of inclusions, to harden the steel by quenching before polishing, because the hardened metal surrounding the inclusions is not so readily worn away and sharper outlines are obtained.[1]

[1] Other methods for the detection and identification of inclusions are described in Appendix III.

Segregation of Impurities — Ghosts. — The very small proportions of impurities generally found in steel of good quality have little, if any, injurious effect upon its most important and useful physical properties, so long as they remain uniformly distributed throughout the metallic mass, i.e. so long as the steel is chemically homogeneous. These impurities, on the contrary, may become extremely injurious when they show a tendency to "segregate," i.e. to collect in certain portions of steel castings and forgings, when the segregated portions may contain so large an amount of impurities as to have their useful properties utterly destroyed. Segregated metal is generally brittle, weak, and hard. Two kinds of segregations should be considered, which may be called respectively major and minor or dendritic segregations. Major segregation results from the assembling of impurities in those portions of castings last to solidify, hence generally in the upper part of the ingot, surrounding the cavity technically called "pipe." This results from the fact that the impurities have generally lower melting points than the metal. Carbon, phosphorus, and sulphur are very prone to segregate in this fashion, and the upper parts of castings frequently contain two or three times as much of these elements as the lower parts. By minor segregation is meant the gathering of impurities in the interstices between the branches or axes of the dendritic crystals already described, and always formed during the solidification of iron and steel. It is also due to the lower melting points of the impurities, the fillings between the axes being the last ones to solidify during these dendritic growths. It might therefore be properly called dendritic segregation. Should the phenomenon of diffusion be carried to completion, each dendrite would become chemically homogeneous, and dendritic segregation, which necessarily accompanies solidification, would cease to exist. This, however, is seldom the case, and dendritic segregation persists. Not only do the interstices between the axes of the dendrites contain more of the impurities, but also a larger proportion, if not the totality, of the inclusions. Moreover, the phosphorus, which probably segregates more than any other impurity, appears to expel the carbon from the fillings, driving it into the axes. The result of this segregation and of this action of phosphorus is to produce dendritic axes containing much carbon, little phosphorus, and few if any inclusions, and of fillings rich in phosphorus and poor in carbon. The working (forging or rolling) of these chemically heterogeneous dendrites results in imparting to the steel a laminated or banded structure readily revealed by suitable etching treatment, which in turn implies different physical properties in a longitudinal direction as compared to those in a transverse direction. Such directional properties are common to all steel forgings, and are the more marked the greater has been the reduction from the casting to the finished article. Under higher magnification, and when it is pronounced, this dendritic segregation altered by work, as just explained, causes the appearance of wide bands known as "ghosts" or "ghost lines." The white bands, which correspond to dendritic fillings elongated by work, are rich in phosphorus, poor in carbon, and generally contain many inclusions, including manganese sulphide.

When forged steel containing ghost lines is heated above its critical range and quenched, the ghost lines are frequently partly eliminated, rarely completely. If the steel is allowed to cool slowly through its critical range, the ghost lines reappear, sometimes in accentuated form. On the assumption that ghost lines are essentially caused by phosphorus segregation, their behavior on heating is explained on the ground that the diffusion of phosphorus needed to efface the lines takes place very

slowly, even at a high temperature, and that although carbon may diffuse readily, it is again thrown out of the phosphorus bands on cooling through the range. Hence ferrite bands rich in phosphorus and containing little carbon are re-formed.

Stead also describes "ghost lines" as lines of ferrite in which are embedded lenticular particles of drawn-out sulphide inclusions, and he adds that when manganese sulphide is found segregated it may be taken for granted that phosphorus also is segregated in the same regions. He believes that the white ferrite lines sometimes observed in forgings are due to phosphorus segregation, the presence of that element having expelled the carbon on slow cooling. He writes that the higher the phosphorus in the steel the thicker and more pronounced are these white carbonless lines in forged steels.

Portevin calls attention to the ferrite which generally surrounds inclusions in slowly cooled hypo-eutectoid steel, and which necessarily intensifies their weakening action. By heating the steel above its Ac_3 or $Ac_{3.2}$ point, the carbon diffuses through those ferrite areas, which on rapid cooling are converted into martensite. The reheating of this martensitic steel to some 600 deg. C. should convert it into sorbite, thus doing away with the ferrite envelope surrounding the inclusions.

Illustrations of banded structure and of ghost lines will be found in Chapter XI, where their occurrence is described at greater length.

Gaseous Impurities. — It has not been possible so far to detect the presence of occluded gases in steel by means of metallographic methods, unless it be the presence of oxygen as FeO and of nitrogen as iron nitride needles. While the problem seems a very difficult one to solve, the statement that it can never be solved would not be justified, for the discovery of some metallographic treatment by which a metal rich in certain gases may be distinguished from a similar metal free from them is well within the limits of reasonable expectation.

The gases present in steel consist chiefly of hydrogen, nitrogen, carbon monoxide, and oxygen, the latter probably as FeO. They are called occluded gases. Some of these gases may be partially eliminated by heating steel in vacuo, when it is noticed that their evolution is more marked at the critical points.

It is probable that nitrogen forms nitrides. It is generally believed to make steel brittle. According to Hoyt, Bessemer steel generally contains 0.015 to 0.030 per cent, and open-hearth steel from 0.001 to 0.008 per cent of nitrogen. It is believed by some and doubted by others, that titanium removes nitrogen from steel by forming a compound with it and transferring it to the slag. The percentage of oxygen in steel is generally determined by the Ledebur method, which detects only the oxygen present as FeO. It is always inferior to 0.10 per cent, while after manganese additions it rarely exceeds 0.025, and may be as low as 0.01 per cent.

CHAPTER VII

THE THERMAL CRITICAL POINTS OF IRON AND STEEL

THEIR OCCURRENCE

The structure of steel described in the preceding chapter, i.e. its normal structure, is greatly affected by the treatment or treatments, both mechanical and thermal, to which the metal may be subjected during the process of manufacture of finished articles. It is chiefly to the close relation existing between the treatment and the structure on the one hand, and between the structure and the physical properties of the metal on the other, that metallography owes its industrial importance. It is essential, therefore, that the student should have a clear understanding of these relations. As a preparation to this important study, however, it will be necessary to describe a phenomenon of the greatest moment in the treatment of steel, namely, the occurrence of spontaneous absorptions or evolutions of heat during the heating or cooling of the metal. These are generally termed the "thermal" critical points or simply "critical points," also "retardations," "transformation" points, and "critical temperatures."

Point of Recalescence. — When a piece of steel containing some 0.80 per cent carbon is heated to a high temperature, say to 1000 deg. C., and allowed to cool slowly from that temperature, and its rate of cooling carefully ascertained, conveniently by means of a Le Chatelier pyrometer, it is found that the cooling proceeds at first at a nearly uniformly retarded rate. If, for instance, it requires 10 seconds for the metal to cool through the first five degrees (from 1000 to 995 deg.), and 12 seconds to cool through the next five degrees (995 to 990 deg.), it will require some 14 seconds for the next five degrees, 16 seconds for the following five, and so on, the cooling through each range of five degrees being a little slower than the preceding cooling of five degrees. All cooling bodies, whatever their nature, generally follow this law. The plotting of time and temperature as coördinates yields smooth curves, sometimes approaching straight lines (see curve B, Fig. 83).

In the case of the steel we are now considering, when a certain temperature is reached, generally at about 700 deg. C., a most interesting and significant phenomenon takes place; the cooling of the metal is momentarily arrested, the pyrometer, for a certain length of time, failing to record any further fall of temperature. Indeed, when the circumstances are favorable, the temperature of the cooling mass actually rises; the metal becomes visibly hotter; it "recalesces," hence the name of "recalescence" given to this thermal critical point. If the experiment be conducted in a dark room, this recalescence or spontaneous glow of the steel is plainly visible. After a while the metal resumes its normal rate of cooling, which is then continued down to atmospheric temperature.

It is evident that at this critical point the surrounding atmosphere does not cease to abstract heat from the piece of steel and, since its temperature nevertheless remains stationary or even rises, it must be that heat is here spontaneously generated within the metal in amount sufficient to make up, or more than make up, for the heat lost by radiation and conductivity.

In heating, as might be expected, the reverse phenomenon takes place: an *absorption* of heat, causing a retardation in the *rise* of the temperature, or even a momentary stop, the pyrometer failing for a few moments to record any further increase of temperature or recording only an abnormally low increase, although heat continues to be applied to the steel at the same speed. Actual *lowering* of the temperature of the steel is not generally observed at this critical point on heating, i. e. the steel does not grow perceptibly cooler.

Notation. — Osmond, who was the first to determine accurately the position and magnitude of the point of recalescence and who is the discoverer of the upper critical points soon to be described, adopted Tschernoff's previous notations, and designated the critical points by the letter A.[1] To distinguish critical points on cooling from those occurring on heating the former are called Ar (r from the French *refroidissement*, meaning cooling) and the latter Ac (c from the French *chauffage*, heating). To distinguish further between the point of recalescence and its reversal on heating on the one hand, and critical points occurring at higher temperatures on the other, the notations Ar_1 and Ac_1 are used for the recalescence point and its reversal, and Ar_2, Ac_2, Ar_3, Ac_3, for the two upper reversible critical points soon to be described. The notations, A_1, A_2, A_3, are frequently used when the points and their reversals are considered collectively. By the notation A_1, for instance, is meant the point of recalescence Ar_1 and its reversal Ac_1. These notations will be used in these pages.

Brinell, in his important work on the heat treatment of steel, used the letter V for the point of recalescence and W for its reversal on heating. These symbols, however, are now very seldom used.

The expression "point of recalescence" is frequently used indifferently for the point on cooling, where heat is evolved causing a recalescence of the metal, and for the reverse phenomenon on heating, at Ac_1, where, of course instead of a recalescence taking place, an absorption of heat occurs causing the metal to *lose* heat. It is obvious that the term "recalescence" should not be applied to the point Ac_1. The point of recalescence is also called sometimes "recalescent" point and, seldom, "Gore's phenomenon" (see Historical Sketch at end of chapter). The point Ac_1 has been called point of "decalescence" by some writers, and one of them at least refers to it as the "calescence" point.

Critical Range — Transformation Range. — When the various critical points occurring in steel are considered collectively, the range of temperature they cover is frequently called the "critical range," or more seldom, but very appropriately, the "transformation range." Critical range in these pages will be used to designate the range of temperature including the A_3, A_2, and A_1 critical points, but not the A_4 or the A_0 points, the former occurring at a considerably higher, and the latter at a much lower temperature, as later explained. The meaning of the expressions "critical range on heating" and "critical range on cooling" is obvious.

Positions of Ar_1 and Ac_1. — The critical points Ar_1 and Ac_1 do not occur at ex-

[1] The point A of Tschernoff indicated the temperature at which steel suddenly acquires hardening properties on heating or loses them on cooling.

actly the same temperature, Ac_1 being generally situated some 20 to 40 deg. higher than Ar_1. When the point Ar_1, for instance, is found at 690 deg. C., the point Ac_1 will generally occur somewhere between 710 and 730 degrees.

Stead submitted samples of very pure steel containing 0.9 per cent carbon to 16 well-known investigators with the request that they ascertain the Ac_1 and Ar_1 points. The reported results indicated for Ac_1 temperatures varying between 719 and 746 deg., and for Ar_1 temperatures between 697 and 721. This apparently great discrepancy may be accounted for in part at least by the influence of the rate of heating and cooling on the positions of Ac_1 and Ar_1 respectively, as later noted, and by the influence of the temperature from which cooling starts on the position of Ar_1. Unless standard conditions are maintained in regard to rate of heating and cooling, temperature from which cooling begins and length of time at that temperature, very close agreement between various investigators is not to be expected.

It is also essential that the temperatures recorded should correspond to exactly the same stage of the critical point, namely its beginning or its apex. Howe argues that the beginning of Ar_1 and Ac_1 should be taken as indicating the position of these points on the ground that the beginning of the transformation is less affected by lag. Rosenhain, on the contrary, and his views are shared by the author, contends that the peaks should be read since they represent the temperatures at which the bulk of the specimen undergoes transformation.

In commercially pure carbon steels Ar_1 almost always occurs between 690 and 720 deg. and Ac_1 some 20 to 40 deg. higher. The fact that the critical point on cooling lags behind the point on heating, and vice versa, is evidently a case of hysteresis so often observed in physical phenomena and which implies a resistance of certain bodies to undergo a certain transformation, when theoretically the transformation is due, the delayed transformation finally taking place with added violence. This has been vividly depicted by Howe, who wrote: "Just as we can cool water below its freezing-point without completely freezing it, thereby rapidly increasing the strength with which the water tends to freeze, so by a relatively rapid cooling we can carry the metal considerably below Ar_1, without giving the Ar_1 change time to proceed far, strengthening the while the tendency toward this change, which keeps kindling more and more till it bursts into a blaze, with such evolution of heat as actually to recalesce, to raise the temperature of the metal by some 10 deg., in spite of the continued abstraction of heat by the continued cooling of the furnace."

The slower the heating and cooling the nearer will the two points approach each other, so that with infinitely slow cooling and heating they would probably occur at exactly the same temperature. If there remained any doubt as to the points Ac_1 and Ar_1 representing the opposite phases of the same phenomenon, i. e. of A being a reversible point, it would suffice to dispel it to consider the fact that in order to induce the retardation Ar_1 the steel must first be heated *past* the point Ac_1; and reciprocally the retardation Ac_1 cannot take place unless the metal has first been cooled to a point below Ar_1. To illustrate: the melting of ice and the freezing of water are undoubtedly the opposite phases of the same phenomenon, each one undoes the work of the other, and in order to freeze the water we must first melt the ice and likewise to melt the ice the water must first be frozen; one change cannot be induced unless the opposite one has last taken place. Indeed it is possible through very slow and undisturbed cooling to lower the temperature of water below its freezing point before it starts freezing, a clear instance of hysteresis, although in this case called

"surfusion," or "undercooling," and when freezing takes place the temperature of the water *rises* to its normal freezing point, a clear case of recalescence although deprived of glow.

The diagram shown in Figure 74 illustrates further this reversibility of the point A_1. Let two parallel lines represent the phases Ac and Ar of the critical point. Let condition *A* represent the state of the metal stable above Ac and condition *B* the state of the metal stable below Ar. The gap between Ac and Ar is due to hysteresis. *MN* is the temperature at which both the Ac point and the Ar point would occur if

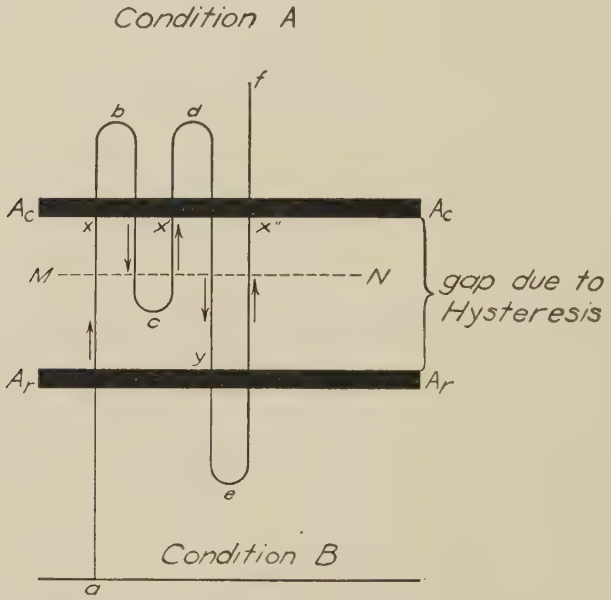


Fig. 74. — Diagram showing reversible critical point.

there were no hysteresis, as for instance if the metal could be heated and cooled infinitely slowly. Assuming the metal to be in condition *B* at *a*, below Ar, on heating it from *a* to *b* above Ac, on reaching the Ac point at *x* it passes from the condition *B* to the condition *A* with absorption of heat, causing a retardation in the heating; on cooling from *b* to *c*, that is to a temperature below Ac but above Ar, the condition *A* is retained so that upon heating from *c* to *d* no transformation can take place at *x'* on passing through the Ac temperature, and therefore no critical point observed. If the metal be cooled from *d* to *e*, however, on passing through Ar at *y* it changes from condition *A* to condition *B* with evolution of heat, causing a retardation in the rate of cooling; if it now be heated again from *e* to *f* above Ac, a critical point will be observed at *x''* since the metal now in condition *B* will pass to condition *A*.

It will be evident that between Ar and Ac the metal may be in condition *A* or condition *B* depending upon whether it was last cooled from above Ac or heated from below Ar.

Howe uses the notation Ae_1 for the equilibrium temperature for A_1, that is for the temperature at which the transformation Ar_1 and its reversal, Ac_1, would both take place, the former on cooling and the latter on heating, in the complete absence of hysteresis. From a very careful weighing of the available data Howe and

also Honda conclude that the position of this equilibrium temperature is probably 723 deg. C.

Speed of Cooling and Heating vs. Position of A_1. — It has been seen that the faster the cooling the lower is the position of the point Ar_1 and the faster the heating the higher the point Ac_1, that is the faster the cooling and heating the greater the gap between the opposite phases Ar_1 and Ac_1 of the reversible point A_1.

The cooling of a piece of steel may be so rapid, to wit in quenching, as to prevent the *full* transformation Ar_1, because it now takes place at a temperature so low that the rigidity of the metal does not permit it, as more fully explained later. In other words, time and a certain amount of plasticity are required for the complete transformation Ar_1 to occur, and in quenching time is denied when the metal is sufficiently plastic (i. e. at a red heat), while when time is given (i. e. after quenching) the metal has lost its plasticity. It remains but partially transformed. It will be shown in another chapter that this lowering of the point Ar_1 is probably the cause of the hardening of carbon steel by sudden cooling.

Le Chatelier rightly reminds us that the speed of the transformations occurring at the critical points of steel follows the general laws which govern the speed of all chemical phenomena. In other words, that the speed of the transformation is the greater (1) the higher the absolute temperature and (2) the wider the range between the actual temperature and the temperature of equilibrium, that is the temperature at which the transformation is due. Above the critical temperature both influences act in the same direction and the speed of transformation increases without limit. Below the critical temperature these influences act in opposite directions, necessarily giving rise to the existence of a maximum speed. According to Le Chatelier this notion of variable speeds of transformation accounts for all the peculiarities of the hardening treatment. On heating it is hardly possible to raise the temperature of transformation more than 100 deg. C. through very rapid heating, while during cooling the speed reaches its maximum at about 600 deg. C., is very feeble below 200, and nearly null at atmospheric temperature.

Temperature from which Cooling begins vs. Position of Ar_1. — It was first observed by Tschernoff that as the temperature to which steel is heated before being allowed to cool increases, the position of the Ar_1 point is gradually, although slowly, lowered. This influence of what Howe calls the maximum temperature or T^{max}, has been repeatedly confirmed. Benedicks would explain it on the assumption that at a higher temperature a greater number of nuclei or centers of crystallization are destroyed and that the fewer nuclei left the lower the temperature at which recalescence occurs. Howe believes that the phenomenon may be further explained (1) through the steepening of the thermal gradient during the critical transformation caused by cooling from a higher temperature, (2) through increase of internal pressure resulting from the steepening of the thermal gradient, and (3) through a better diffusion of the proeutectoid element and the pearlite element, so that their re-assembling for the purpose of undergoing the transformation in cooling is more difficult.

A long sojourn at a high temperature also appears to have a tendency to lower Ar_1, while according to Rosenhain the position of Ac_1 is slightly raised if the previous cooling has been very slow and vice versa.

Chemical Composition vs. Position of A_1. — Some impurities have a tendency to lower the position of Ac_1 and Ar_1, others to raise it.

According to Howe, manganese lowers the Ar_1 point some 24 to 50 deg. C. for each

per cent of manganese, while Osmond indicates the position of Ar_1 in a steel containing 1 per cent of Mn as 685 deg. whereas with 4 per cent of manganese the same point was lowered to 590 deg. It is conceivable that further increase of that element must lower still more the critical point, so that finally it may be lowered below atmospheric temperature, being apparently eliminated. It will be shown in another chapter that this is precisely what occurs in the cases of manganese steel and high nickel steel, containing respectively some 13 per cent of manganese or some 25 per cent of nickel. These steels exhibit no retardation on cooling from a high temperature to atmospheric temperature. When cooled to lower temperatures, however, by immersing them in freezing mixtures or, if need be, in liquid air, the retardations may again occur, at least in the case of nickel steel.

G. H. Clevenger found that 4.5 per cent copper lowers the Ar_1 point of steel containing some 0.5 per cent carbon from 730 to 635 deg. C. or approximately 20 deg. for each per cent of copper. According to J. H. Andrews the absorption of 0.25 per cent of nitrogen by a steel containing 0.6 per cent carbon lowers the point Ar_1 in a marked degree. Silicon and chromium, on the contrary, raise the point Ac_1.

In the case of commercial steel of good quality the proportion of impurities, with the possible exception of manganese, varies within relatively very narrow limits, so that no great variation should be expected in the position of the critical point A_1. Neither is it clear that the amount of carbon present in steel has a marked effect upon the position of the point A_1, although some writers state that the point is lifted as the carbon increases. As previously stated, in pure carbon steel the point Ar_1 almost invariably occurs somewhere between 690 and 720 deg. C. and its reversal Ac_1 20 to 40 deg. higher. Both Ar_1 and Ac_1 would probably occur at about 720 deg. could the cooling and heating be infinitely slow.

Upper Critical Points. — The existence of upper critical points, that is of thermal retardations occurring at temperatures higher than that of the recalescence point, has already been alluded to. These points were discovered by Osmond and their discovery ushered in a new epoch in the scientific study of iron and steel. To describe these points it is advisable to consider first the thermal retardations occurring in cooling and heating carbonless iron and then similar retardations exhibited by steel containing increasing amounts of carbon.

Thermal Critical Points in Pure Iron. — On cooling from a high temperature, say 1000 deg. C., a piece of the purest iron obtainable and ascertaining its rate of cooling as previously explained, the metal is found to cool normally, i.e. at a uniformly retarded rate, until a temperature of some 900 deg. C. is reached, when a marked retardation is observed in the rate of cooling, indicating a spontaneous evolution of heat, in this case, however, insufficient to cause an actual rise of temperature, i.e. a recalescence of the metal. The cooling then resumes, or nearly resumes, a normal rate of cooling, until at about 770 deg. C. a second evolution of heat takes place, causing another retardation in the rate of cooling, not so marked, however, nor so sharply defined as the first one. The metal then cools normally or quite so to atmospheric temperature. We have thus detected two unmistakable spontaneous evolutions of heat in the cooling of pure iron. The corresponding critical points are called Ar_3 and Ar_2, the latter symbol indicating the lower point. It should be noted that the recalescence point, which should occur at some 700 deg., is here absent. Carbonless iron has no point of recalescence.

These two upper points like the point of recalescence are reversible critical points,

i.e. on heating, the opposite phases of the transformations (whatever those transformations may be) take place with absorption of heat, causing a retardation in the rate of heating and the corresponding points being designated by the symbols Ac_3 and Ac_2. The point Ac_3 occurs at a temperature some 10 to 30 deg. higher than its reversal Ar_3, while Ac_2 occurs at nearly the same temperature as Ar_2.

Dr. J. K. Burgess and J. J. Crowe (Bulletin American Inst. Mining Engineers, October, 1913, p. 2537) made a large number of determinations of the critical points of the purest irons obtainable, using great refinement in manipulations, and found Ac_3 to occur at 909 deg. C., Ar_3 at 898 deg., and Ac_2 and Ar_2 both at 768 deg.

Peculiarities of the Point A_2. — The point A_2 is generally less marked than the points A_3 and A_1. Unlike A_3 its position is little affected by the carbon content, and unlike A_3 and A_1 the point on heating, Ac_2, occurs at nearly the same temperature as the point on cooling, Ar_2. To these peculiarities must be added another one, namely, the fact that A_2 appears to cover a wide range of temperature. While its intensity decreases with fall of temperature its lower limit probably extends to considerably below 700 deg. In other words, the transformation of which A_2 is a manifestation is not completed by the time the point A_1 is reached. Indeed Osmond mentions 550 deg. C. as the probable lower limit of the point A_2, while Honda and others claim that the Ac_2 transformation starts at room temperature and that the absorption of heat at Ac_2 marks its *end*; and likewise that the Ar_2 point marks the *beginning* of the opposite transformation ending at room temperature. These views are considered at greater length in the following chapters.

Thermal Critical Points in Very Low Carbon Steel. — Let us now take a sample of steel containing some 0.10 per cent carbon, and let us ascertain its rate of cooling from a high temperature precisely as before. Three thermal retardations will be detected, Ar_3 at about 850 deg., Ar_2 near 770 deg., and Ar_1 (point of recalescence) near 700 deg. Of these three spontaneous evolutions of heat the upper one at Ar_3 will be the most marked, while at Ar_2 and at Ar_1 they will be quite faint, their satisfactory detection calling for the use of delicate instruments and careful manipulations. On heating, corresponding retardations will occur, due to spontaneous absorptions of heat, the resulting critical points being designated as Ac_3, Ac_2, and Ac_1. Of these Ac_3 and Ac_1 will occur at temperatures some 20 deg. or more higher than Ar_3 and Ar_1, while Ac_2 will occupy nearly the same position as Ar_2 on the temperature scale, that is about 760 deg.

Thermal Critical Points of Medium High Carbon Steel. — The determination of the rate of cooling of a steel containing some 0.45 per cent carbon reveals the existence of two critical points, one, evidently the point of recalescence, Ar_1, at the usual temperature (680 to 720 deg.), and one upper point in the vicinity of 740 deg. Does the presence in this steel of only one upper point mean that one of the two upper points detected in carbonless iron and in very low carbon steel has disappeared, because of the presence of more carbon, or does it mean that the two upper points have now united into a single one? The latter view is generally assumed to be the correct one and this single upper point of medium high carbon steel is designated accordingly by $Ar_{3\cdot2}$. This notation clearly implies that the two distinct evolutions of heat which in carbonless iron and in very soft steel occur separately at Ar_3 and Ar_2 here occur at one and the same temperature. Increasing the carbon content decreases the interval of temperature between the two upper points until, finally, for a certain carbon content the points meet to form the double point $Ar_{3\cdot2}$.

Merging of A_3 and A_2. — It has been seen that as the carbon increases, the point A_3 is gradually lowered until finally it merges with A_2, whose position is not greatly affected by the presence of carbon, to form the point $A_{3\cdot2}$. It would be interesting to know the exact proportion of carbon required to cause this merging. This, however, is difficult to ascertain because of the experimental difficulty of separating two critical points situated very near each other, as they must be in the vicinity of the merging point, and also because this merging will be shifted somewhat by speed of heating and cooling and by slight changes of chemical composition. According to A. Meuthen's calorimetric work later referred to, A_3 and A_2 merge for a carbon content corresponding to 0.32 per cent, while Howe indicates 0.438 per cent carbon as the probable merging point. From the mass of experimental evidences which have been published it seems probable that in commercial steels the merging takes place at about 0.35 per cent carbon.

Equilibrium Temperatures for A_3 and $A_{3\cdot2}$. — Howe uses the notations Ae_3 for the equilibrium temperature for A_3, that is the temperature at which the transformation Ar_3 on cooling and its reversal, Ac_3 on heating, would take place in the complete absence of hysteresis. A close examination of the available data leads to the conclusions that the position of Ae_3 is given by the formula

$$T^\circ = 917 - 306 \times C$$

in which C represents the percentage of carbon in the steel and T° the temperature in degrees C. for Ae_3.

For the equilibrium temperature of $A_{3\cdot2}$ Howe gives the formula

$$T^\circ = 820 - 105.5 \times C$$

Thermal Critical Point in Eutectoid Steel. — As already noted, eutectoid steel, that is steel containing some 0.85 per cent of carbon, exhibits but one critical point, the point of recalescence, very marked at about 700 deg. C. on cooling. Shall it be inferred from the occurrence of this single point that in eutectoid steel the transformations of which the upper points A_3 and A_2 or the double point $A_{3\cdot2}$ are manifestations do not take place? Or shall it be assumed that these transformations now take place at the same temperature as the transformation corresponding to the critical point A_1? In other words, that increasing the amount of carbon has so depressed the position of the two upper points as to cause them to unite with the lower point, forming now a triple point, to be designated as $Ar_{3\cdot2\cdot1}$? This is the view generally held. The critical point on heating is designated by the notation $Ac_{3\cdot2\cdot1}$. It will be explained in another chapter why the points A_3, A_2, or $A_{3\cdot2}$ cannot exist in eutectoid or hypereutectoid steel, when it will also be shown that it can be contended that the single point of eutectoid steel is not in fact a merging of A_3, A_2, and A_1, but merely the point A_1, the upper points having disappeared.

Merging of $A_{3\cdot2}$ and A_1. — As the carbon content of the steel increases still more after the merging of A_3 and A_2 has been effected, the interval between the points $A_{3\cdot2}$ and A_1 gradually diminishes until these two points, in turn, appear to merge to form the triple point $A_{3\cdot2\cdot1}$. Theoretically this apparent merging should occur when the steel is composed entirely of pearlite, that is when it contains in the vicinity of 0.85 per cent carbon, for reasons that will later be made clear. As a matter of fact, however, the merging seems to take place long before so large a proportion of carbon is present, for the point $A_{3\cdot2}$ is seldom detected in steel containing more than some

0.50 or 0.60 per cent of carbon; this is probably due, as already explained, to the difficulty of separating, experimentally, two critical points so close to each other.

Factors Influencing the Positions of the Upper Points A_3 and A_2. — It has been made clear that as the carbon increases the point A_3 is gradually lowered until with some 0.30 or 0.40 per cent carbon it merges with the A_2 point, while the resulting double point $A_{3\cdot2}$ is further lowered with increasing carbon and merges with the A_1 point at about 0.85 per cent carbon. The position of the A_2 point, on the contrary, so long as that point remains independent, that is in alloys containing less than some 0.40 per cent carbon, is unaffected by variations in carbon content. Like the points of recalescence, the upper points on cooling, Ar_3, Ar_2, and $Ar_{3\cdot2}$, are probably lowered (1) by rapid cooling, (2) by increasing the temperature from which cooling starts, (3) by a long sojourn at a high temperature, and (4) by the presence of notable proportions of some elements such as manganese and nickel, while the corresponding points on heating, Ac_3, Ac_2, and $Ac_{3\cdot2}$, are probably slightly raised by increased speed of heating.

P. Oberhoffer reports that one per cent of manganese lowers the point A_3 or $A_{3\cdot2}$ about 70 deg. C., while Charpy and Cornu-Thénard (Comptes Rendus, 1913, Vol. CLVII, p. 319) found (1) that the point A_3 of iron and low carbon steel vanishes when the silicon-content reaches 1.5 per cent and (2) that the point A_2 remains distinct but that each increase of one per cent of silicon lowers its position by about 11 deg. C.

Thermal Critical Points in Hyper-Eutectoid Steel. — Carefully conducted observations reveal the existence of an upper critical point in hyper-eutectoid steel, at least in steel containing a decided amount of free cementite and, of course, of the point of recalescence. It seems proper to designate this upper point by the symbol A_{cm} (Ar_{cm} on cooling, Ac_{cm} on heating) for reasons later to be given, cm standing for cementite. At least one writer, however, has designated this point on cooling by the notation Ar_{mc}, mc standing for massive cementite. Other writers have called it an A_3 point, a notation from which one would naturally infer that this upper point of hyper-eutectoid steel is similar to the upper point of iron and of very low carbon steel, which is not the case.

Purely theoretical considerations lead us to infer that the position of the point A_{cm} is lowered as the proportion of carbon decreases, finally merging with the point $A_{3\cdot2\cdot1}$ at the eutectoid point. It would follow from this that the single point of eutectoid steel is really a merging of four points A_3, A_2, A_1, and A_{cm} and that it should accordingly be designated by $A_{3\cdot2\cdot1\cdot cm}$. It is, however, the universal custom to ignore this contribution of A_{cm} to the single point of eutectoid steel and to use for the latter the notation $A_{3\cdot2\cdot1}$.

The amount of heat evolved at Ar_{cm} is very slight, hence the difficulty of detecting this point. Carpenter and Keeling ascertained its existence in steels containing respectively 1.31, 1.51, 1.69, 1.85, and 1.97 per cent carbon at the following corresponding temperatures: 883, 911, 985, 1030, and 1042 deg. C. With lower carbon contents, that is nearer the eutectoid composition, the heat evolved is so slight that the detection of Ar_{cm} as a separate point is quite impossible. In theoretical diagrams, however, the existence of this point is always indicated in all hyper-eutectoid steels with a sharp merging with $A_{3\cdot2\cdot1}$ at the eutectoid point.

The point Ar_{cm} then should occur in all hyper-eutectoid steels at temperatures increasing from some 700 to 1050 deg. C. as the carbon increases from 0.85 to 2.00 per cent.

Merging of $A_{3\cdot2\cdot1}$ and A_{cm}. — As already explained theoretically the merging of the points $A_{3\cdot2\cdot1}$ and A_{cm} should take place at the eutectoid composition, that is for steel containing in the vicinity of 0.85 per cent carbon. Experimentally, however, the point A_{cm} cannot be detected in steel containing less than some 1.20 per cent carbon. Bearing in mind that hypo-eutectoid steels containing more than 0.60 per cent carbon or thereabout have likewise but one thermal critical point so far as experimental evidences are concerned, it will be seen that for all practical purposes we may consider all grades of steel containing from 0.60 to 1.20 per cent carbon as having but one critical point, namely, the point of recalescence, at some 700 deg. C. on cooling, although theoretcially eutectoid steel only has but one such point. The existence of the A_0 critical point soon to be described is not considered here.

Data Showing the Position of the Critical Points. — A very comprehensive set of determinations of the critical points of iron and steel was made by Carpenter and Keeling. Their results are tabulated on the following page. The table includes the critical points occurring during the soldification period of the various steels and irons investigated. These will be considered in another chapter. The position of the critical points as determined by Burgess, Stead, and others has already been indicated. There is substantial agreement between the results of these investigators.

Relative Quantities of Heat Evolved or Absorbed at the Critical Points. — The various critical points that have been considered in the preceding pages do not indicate evolutions or absorptions of equal quantities of heat; they are not of equal intensity. The point A_3 is very marked and sharply defined in carbonless iron but decreases rapidly in intensity as the carbon increases. The point A_2 is relatively feeble and not very sharply defined, and as already mentioned shows a tendency to cover a considerable range of temperature. Its intensity, moreover, is little affected by the carbon content of the steel. The point $A_{3\cdot2}$, being a merging of A_3 and A_2, is more intense than A_2 but less intense than A_3 in carbonless iron owing to the fact that when the merging takes place the A_3 point has lost much of its intensity. The point A_1 is feeble in very low carbon steel, but its intensity increases rapidly with the carbon content, becoming so great as to cause the metal to glow or recalesce as previously described and being maximum for steel of eutectoid composition. These differences in the thermal values of the critical points will be explained in another chapter.

A. Meuthen (Ferrum, 1912, Vol. X, p. 1) found by careful calorimetric experiments (1) that one gram of pearlite requires 15.9 calories for its transformation into austenite (a transformation which occurs at Ac_1 or $Ac_{3\cdot2\cdot1}$, as explained in the following chapter); (2) that the transformation of one gram of β iron into α iron develops 5.6 calories (a transformation which occurs at Ar_2); (3) that the transformation (at Ar_3) of one gram of γ iron into β iron also develops 5.6 calories; and (4) that the separation of one gram of α iron (free ferrite) from the solid solution (austenite), a separation which occurs *between* Ar_3 and Ar_1, produces 14.1 calories.

Graphical Representation of the Position and Magnitude of the Critical Points. — The position of the critical points corresponding to various percentages of carbon is illustrated graphically in Figure 75. The diagram refers to the critical points on cooling, i.e. the Ar points, and it should be borne in mind that the corresponding points on heating, the Ac points, occur some 20 to 40 deg. higher, with the exception of the point Ac_2, which seems to occupy nearly the same position as the point Ar_2. An attempt has been made in this diagram to indicate the relative intensities of the

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Alloy No.	Carbon per Cent.	Range of Solidification.		Ar.m.c.	Ar3		Ar2.		Ar1.	
		Beginning.	End.	Beginning.	Beginning.	Maximum.	Beginning.	Maximum.	Beginning.	Maximum.
1	0·01	...	...	...	901	900	784	762	...	...
2	0·02	1504*	1470*	...	900	890	795	762	...	...
3	0·05	...	...	...	905	884	780	762	...	...
4	0·12	1504†	1470†	...	894	838	774	762	693	688
5	0·16	1498†	1465†	...	872	837	771	762	697	693
6	0·17	1497†	1450†	...	...	...	...	...	...	...
7	0·24	1492†	1448†	...	890	Merged	...	762	696	693
8	0·38	1479†	1416†	...	...	...	778	762	700	699
9	0·47	1482†	...	...	...	...	777	762	...	703
10	0·53	1473†	1404†	...	...	...	762	730	...	700
11	0·61	1469†	1394†	...	...	...	780	Merged	Merged	699
12	0·80	1457‡	1351‡	...	...	...	...	...	...	(704)
13	0·80	1454†	...	...	...	...	...	...	...	(695)
14	0·81	1460†	1351†	...	774	Merged	...	Merged	Merged	706 (705)
15	0 93	1443†	...	...	774	,,	...	,,	,,	699
16	1·31	1426†	1286†	883	774	,,	...	,,	,,	(711) 695
17	1·51	1406†	1244†	911	768	,,	...	,,	,,	(713) 684
18	1·69	1388†	...	985	774	...	...	...	...	(708) 710
19	1·81	1383†	...	...	...	...	...	...	...	...
20	1·85	1383†	1179†	(1015) 1030	783	Merged	...	Merged	Merged	(711) 711
21	1·97	1367†	...	(1042)	...	...	...	...	...	(710)
22	2·12	1350†	1110†	...	...	...	...	...	...	(714)
23	2·21	1354†	1107†	...	801	Merged	...	Merged	Merged	714
24	2·25	1352†	1122†	...	...	...	...	...	...	...
25	2·25	1348†	1122†	...	...	...	...	...	...	(714)
26	2·47	1330†	1134†	1035	801	Merged	...	Merged	Merged	708
27	2·63	1305†	...	1040	801	...	...	...	...	716
28	2·67	1306†	...	...	...	...	...	...	...	...
29	2·74	1300†	1139†	...	...	...	...	...	...	...
30	2·85	1292†	1139†	1058	...	Merged	...	Merged	Merged	716 (715)
31	3·03	1277†	1139†	...	777	,,	...	,,	,,	702 (717)
32	3·29	...	1141†	...	...	...	...	...	...	...
33	3·42	1238†	1114†	1058	790	Merged	...	Merged	Merged	703 (714)
34	3·51	1230†	1136†	...	...	...	...	...	...	...
35	3·87	1190†	1144†	1090	770	Merged	...	Merged	Merged	(716) 716
36	3·98	1171*	1138*	1087	...	...	...	...	...	713
37	4·37	1136*———	———1136*	...	...	...	...	...	...	(714)
38	4·50	1146*———	———1146*	1087	777	Merged	...	Merged	Merged	715

* Thermojunction M_5 platinum platinum 10 per cent iridium.
† " M_5 " " " "
‡ " M_4 " " " rhodium.

The temperatures in brackets in columns 5 and 11 were obtained by direct cooling. All other temperatures in columns 5–12 were obtained by differential cooling.

Ar.m.c. represents separation of massive cementite.
Ar3 " change from γ to β iron.
Ar2 " " " β to α "
Ar1 " " " hardening carbon to pearlite carbon.

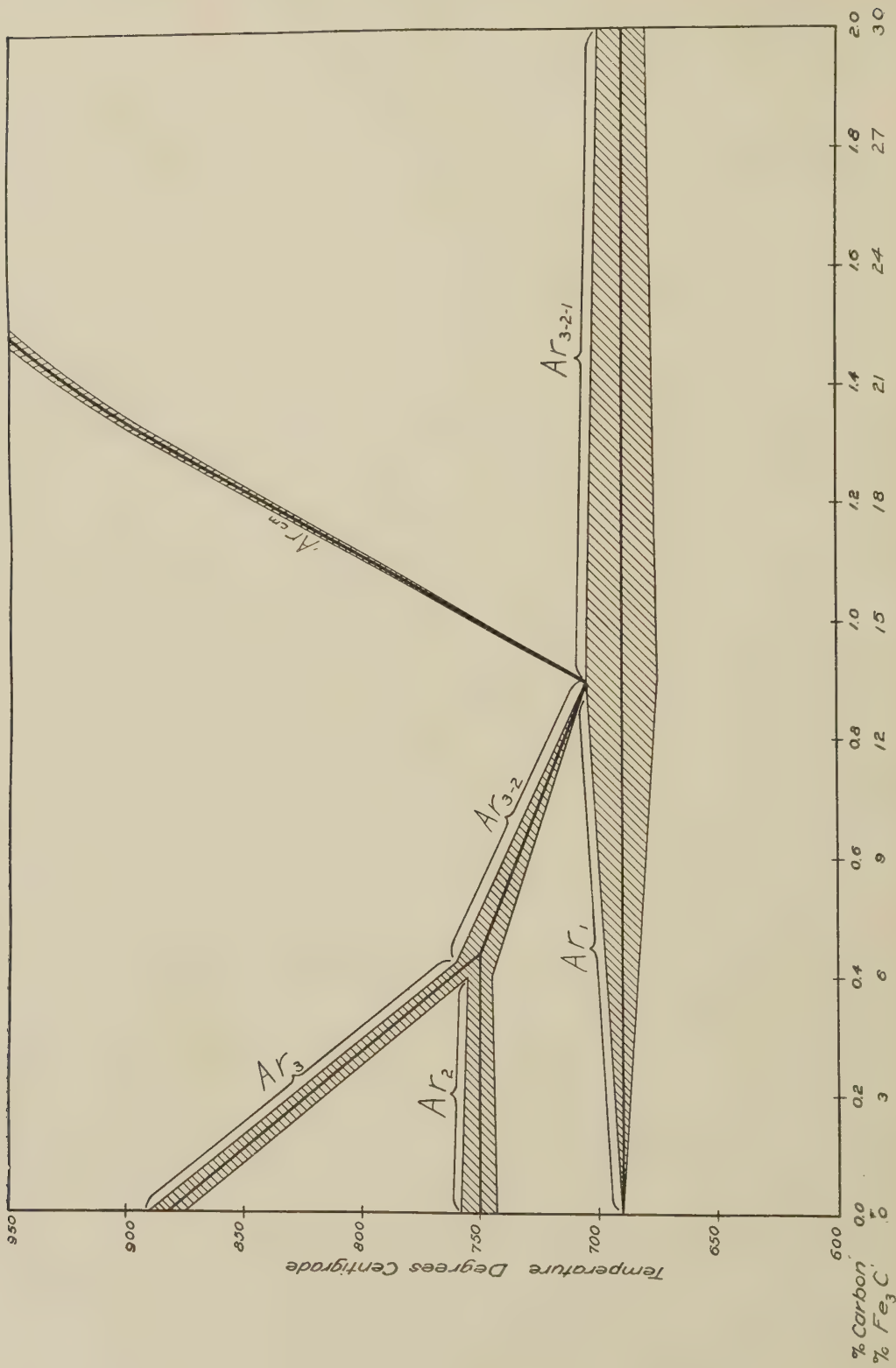


Fig. 75. — Diagram showing the position and magnitude of the critical points.

various points by shaded areas of proportional thickness on both sides of the lines indicating their position. This is based chiefly on theoretical considerations and is in accordance with the generally accepted views regarding the causes of the critical points as explained in the next chapter. An examination of the diagram shows (1) that the point Ar_3 intense in carbonless iron decreases gradually in intensity as the carbon increases, (2) that the intensity of Ar_2 is not greatly affected by the carbon content, (3) that $Ar_{3\cdot2}$ fairly intense at first becomes rapidly feebler and finally disappears just as it meets Ar_1, (4) that Ar_1 at first very faint becomes more marked

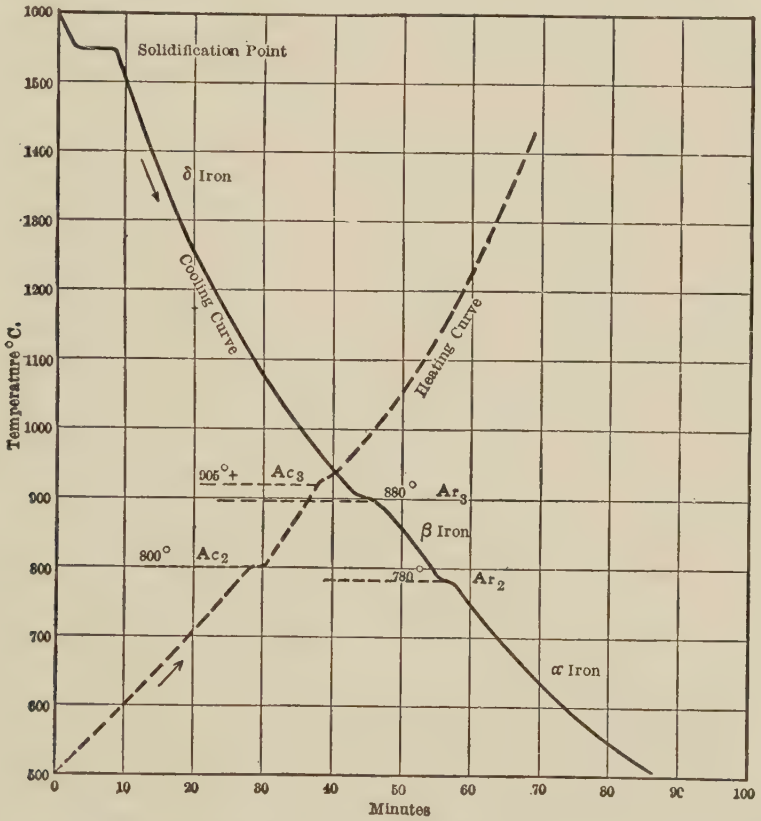


Fig. 76. — Time-temperature curves. Heating and cooling of pure iron. (Gœrens.)

with increased carbon, being maximum for a carbon content of some 0.85 per cent (the eutectoid point), (5) that the point $Ar_{3\cdot2\cdot1}$ very intense at the eutectoid point gradually loses some of its intensity, although always remaining pronounced, and (6) that the point Ar_{cm} very faint near the eutectoid composition increases in intensity with the carbon content.

These theoretical inferences are well supported by experimental evidences in the case of the magnitude of the points Ar_1 and $Ar_{3\cdot2\cdot1}$ and quite satisfactorily in regard to Ar_3 and Ar_{cm}. They ascribe to the points Ar_2 and $Ar_{3\cdot2}$, however, a magnitude and a sharpness which is not borne out by experiments, as later explained, when it will also be seen that some writers doubt the accuracy of the explanation generally offered to account for the point A_2.

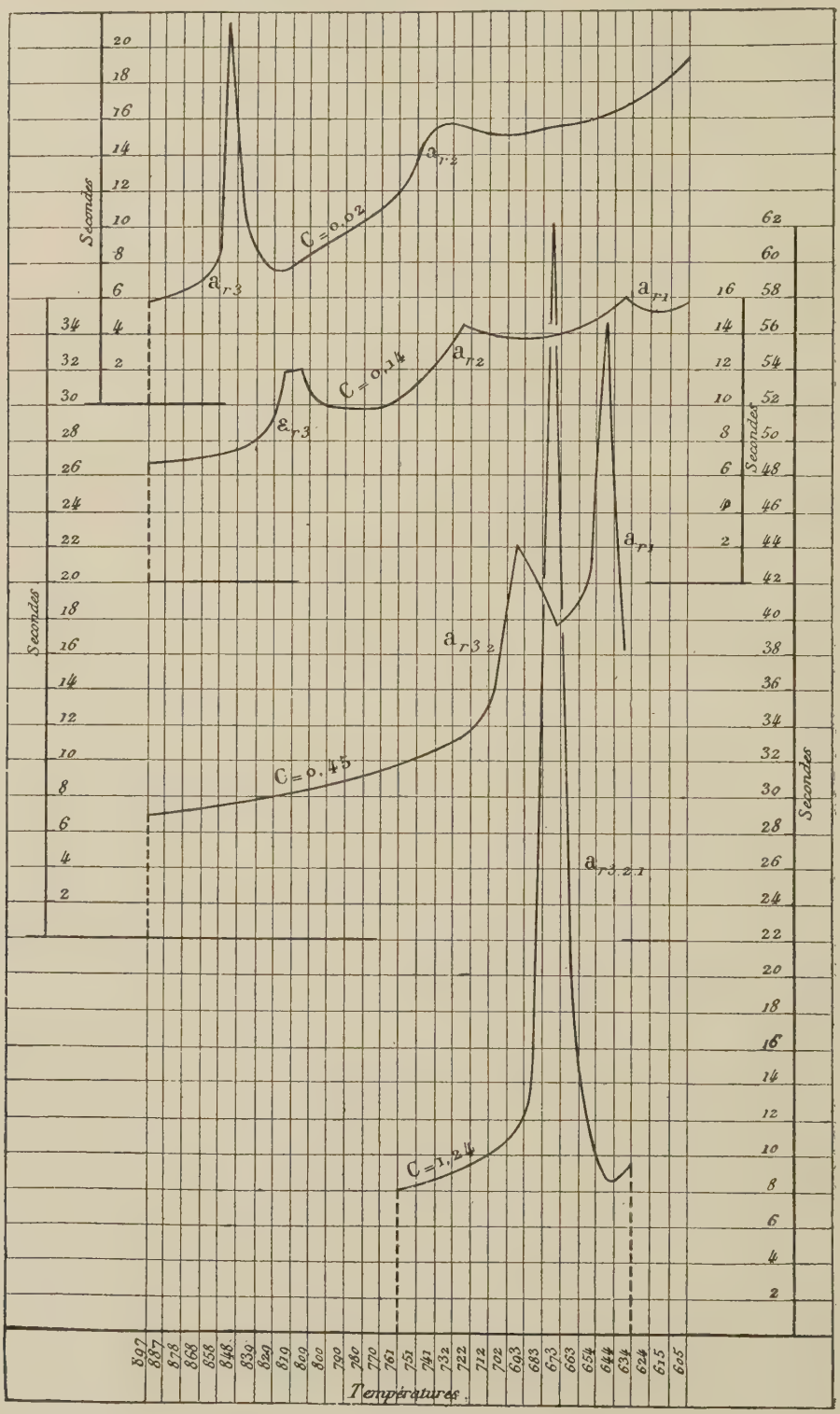


Fig. 77. — Inverse rate curves. Cooling of steels containing respectively 0.02, 0.14, 0.45, and 1.24 per cent carbon. (Osmond.)

Determination of the Thermal Critical Points. — The thermal critical points are generally determined by means of a Le Chatelier thermo-electric pyrometer. Indeed it is the invention of this invaluable instrument that made the detection of the upper critical points possible. Had it not been invented we probably would still be in ignorance of the existence of the upper points.

Cooling and Heating Curves. — The determination of the thermal critical points calls for the construction of heating and cooling curves. In these curves successive falls (or rises) of temperature, say of 10 deg. C., $\theta - 10$, $\theta - 20$, $\theta - 30$ . . . are plotted as ordinates, while as abscissæ are plotted (*a*) the corresponding time intervals in seconds, t, t′, t″, t‴ . . . elapsed since the beginning of the observation, or (*b*)

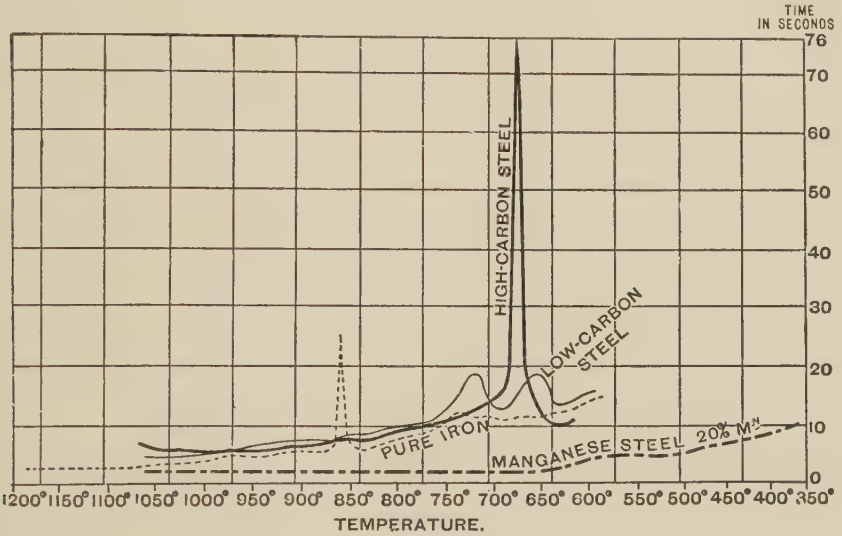


Fig. 78. — Inverse rate curves. Cooling of pure iron, low carbon steel, high carbon steel, and manganese steel. (Roberts-Austen.)

the actual intervals of time t′ − t, t″ − t′, t‴ − t″ . . . required for each noted fall of temperature. In other words the coördinates are θ and t in the first instance, θ and dt in the second. The curve obtained by the first method is known as a time-temperature curve while the second method yields an inverse rate curve.[1]

Time-temperature curves representing the heating and cooling of pure iron are shown in Figure 76. While in these curves the evolutions or absorptions of heat corresponding to the points A_3 and A_2 can be detected, they do not stand out very conspicuously, and it may well be feared that slight thermal retardations might escape detection in curves of this kind since they would cause but very slight jogs. These considerations led Osmond to adopt the inverse rate method for the plotting of thermal curves. Curves of this type are shown in Figures 77 and 78. The thermal points correspond to sharp peaks in the curves, the lengths of which are roughly proportional to the amount of heat evolved on cooling or absorbed on heating. This method

[1] It is evident that similar curves would result from reversing the observations, i.e. noting the successive falls of temperatures θ, θ', θ'' . . . corresponding to equal intervals of time, say of 15 seconds, t + 15, t + 30, t + 45 . . . and plotting the former as ordinates and the latter as abscissæ. The coördinates in this case would be $d\theta$ and t.

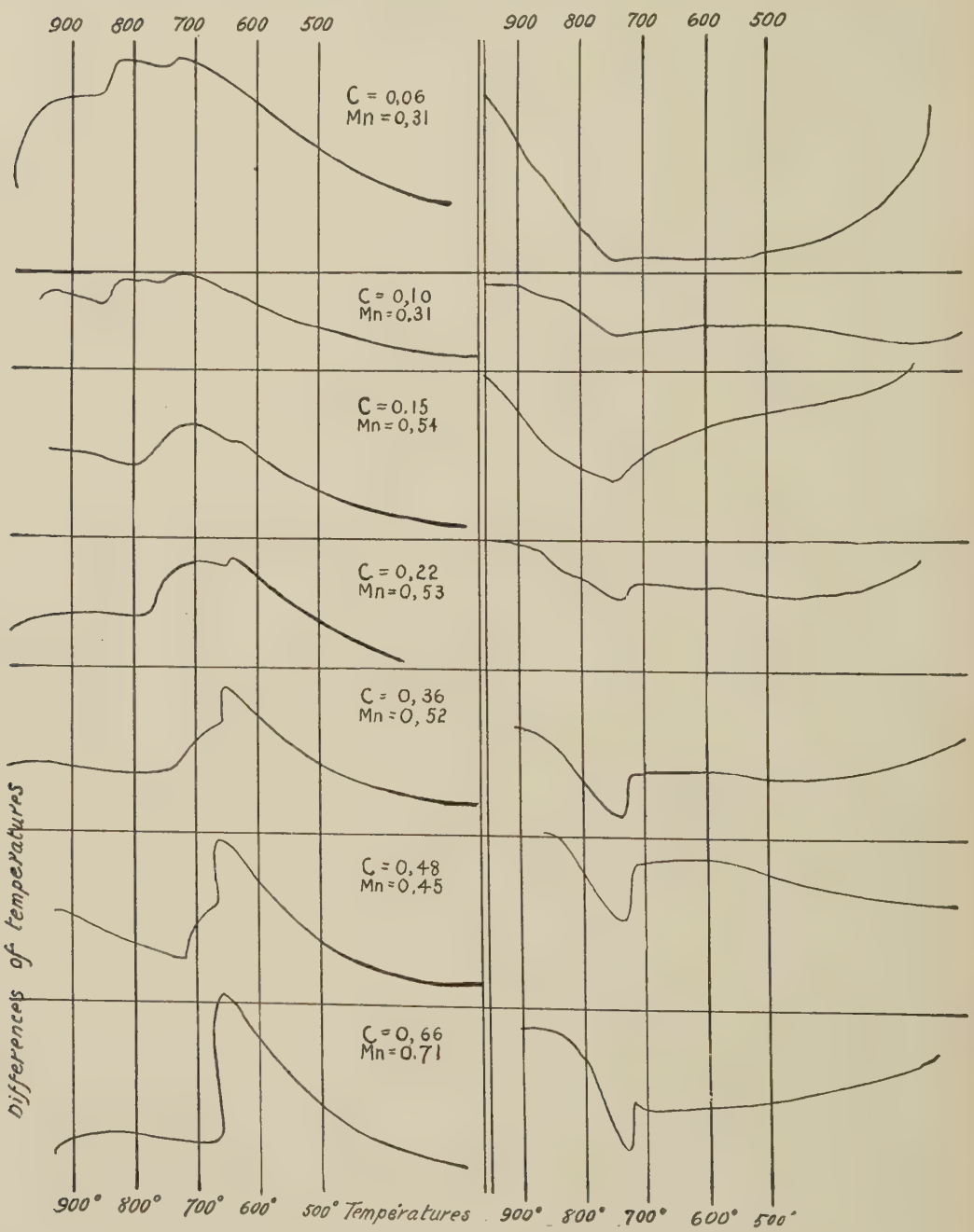


Fig. 79. — Difference curves. Cooling and heating of various steels. (Saladin.)

is quite universally applied unless, as later explained, a neutral body is used for the determination of the critical points.

Use of Neutral Bodies. — The method described above for the detection of the thermal critical points is open to the objection that the rate of cooling or heating of the steel under observation is necessarily affected by any irregularity in the cooling

or heating of the furnace itself and by other outside agencies. These disturbing factors introduce irregularities in the thermal curves which may render their interpretation difficult and may indeed altogether hide the existence of critical points where but a very small amount of heat is evolved or absorbed. Again on cooling, for instance, when a critical point is reached the temperature of the metal is affected in opposite directions (1) by the cooling furnace, which has a tendency to lower its temperature, and (2) by the evolution of heat occurring at the critical point, the effect of which is to raise its temperature. It is evident that the cooling influence of the furnace has a tendency to decrease the apparent magnitude of the critical point and therefore to mask it.

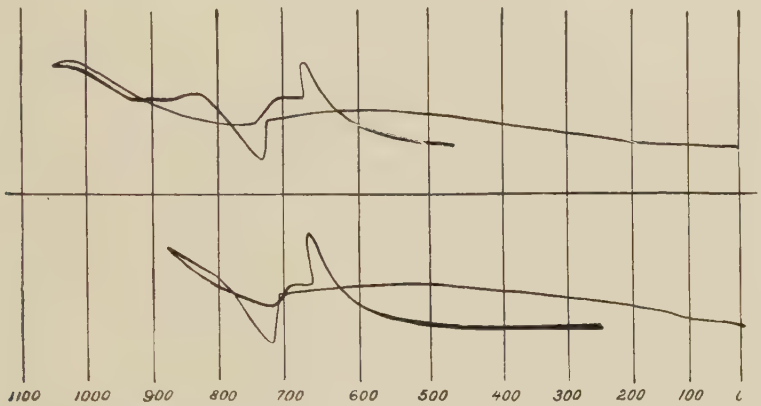


Fig. 80. — Difference curves. Cooling and heating curves taken on same photographic plate. (Saladin.)

The elimination of these objectionable influences should result in sharper thermal curves and in the detection of faint evolutions or absorptions of heat. This was accomplished by Roberts-Austen through the use of a neutral body and double thermocouple so connected that the difference of temperature between the metal under investigation and the neutral body is recorded, as well as the actual temperature of the metal. If the heat capacities and emissivities of the metal and of the neutral piece were identical, their temperature would be exactly the same except at the critical points, when heat is evolved or absorbed by the metal, while the neutral body is, of course, free from any such thermal disturbance. Any difference of temperature between the two pieces, therefore, would indicate a critical point. Since it is generally impossible, however, to use a neutral body having exactly the same heat capacity as that of the metal under observation, it will be apparent that there will always be a difference between the temperatures of the two pieces, one always lagging behind the other, and that the critical points will correspond to sudden increase in the difference between their respective temperatures. Since, however, the critical points are now caused solely by abrupt differences between the temperatures of the two bodies, they are freed from the irregularities mentioned above as well as from the masking influence of the falling or rising temperature of the furnace, seeing that both pieces are now equally affected, and the curves obtained should indicate more sharply the existence of even faint absorptions or evolutions of heat.

The neutral body should, of course, be free from any transformation within the

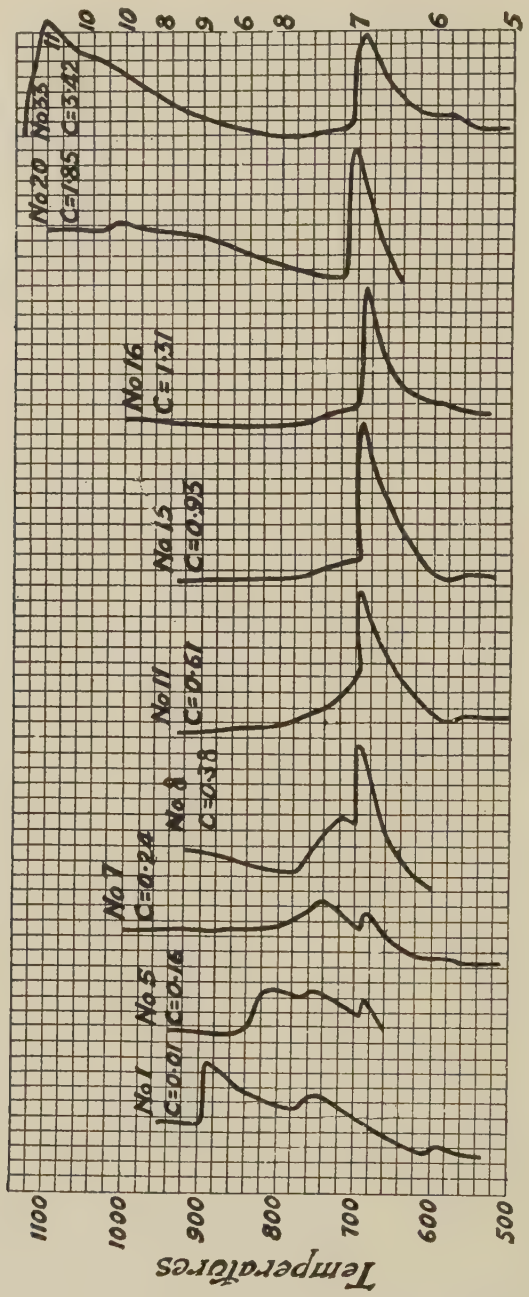


Fig. 81. — Difference curves. Cooling of a series of very pure carbon steels. (Carpenter and Keeling.)

range of temperature covered by the experiments. Platinum, porcelain, clay, 25 per cent nickel steel, and (by the author) austenitic manganese steel have been used. The plotting of the thermal curves when a neutral body is used may be done in two different ways, (1) successive falls (or rises) $\theta - 10$, $\theta - 20$, $\theta - 30$ . . . of the temperature of the metal as indicated by one of the galvanometers may be plotted

as ordinates against the corresponding differences in temperature $\theta - \theta_1$, $\theta' - \theta'_1$, $\theta'' - \theta''_1$ . . . of the two cooling bodies, as indicated by the second galvanometer, the coördinates in this case being θ and $\theta - \theta_1$, and the curve known as a "difference"

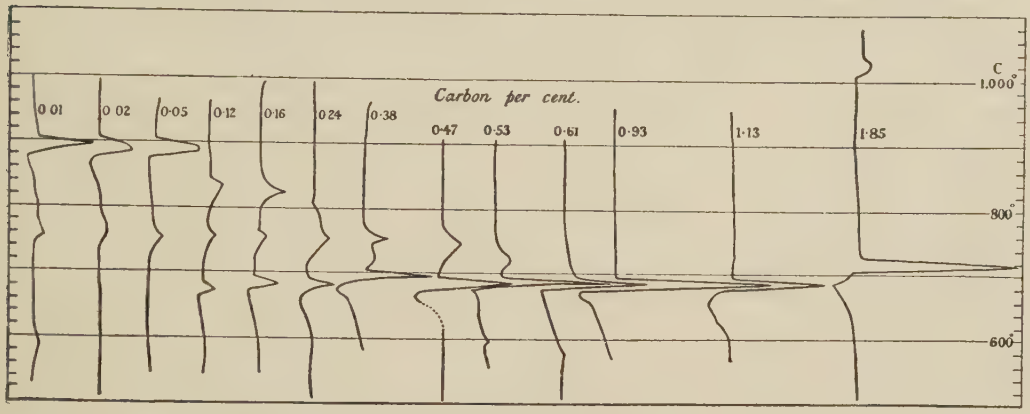


Fig. 82. — Derived differential curves of carbon steels replotted from the data of Carpenter and Keeling. (Rosenhain.)

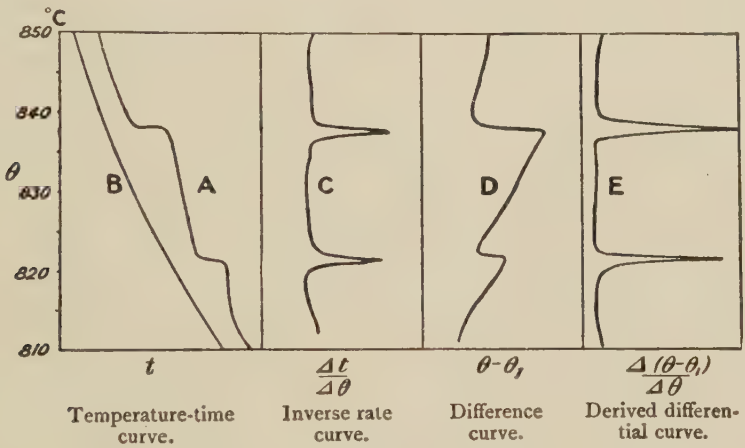


Fig. 83. — Different types of cooling curves. (Desch.)

curve, or (2) according to Rosenhain, successive falls of temperature may be plotted as ordinates against the corresponding *rate of cooling for each degree of temperature* $\frac{\theta - \theta_1}{\theta}$, $\frac{\theta' - \theta'_1}{\theta'}$, $\frac{\theta'' - \theta''_1}{\theta''}$ as abscissæ, the coördinates being in this method θ and $\frac{\mathrm{d}(\theta - \theta_1)}{\mathrm{d}\theta}$ and the curve known as a "derived differential" curve.

Difference curves are shown in Figures 79 to 81. The curves of Figures 79 and 80 were taken with a Saladin-Le Chatelier-Pellin instrument. Figure 79 shows the critical points on heating and cooling of a series of carbon steels containing from 0.06 to 0.66 per cent carbon, the cooling and heating curves having been taken on separate photographic plates. In Figure 80 are shown the heating and cooling curves taken on the same plate of two steels containing respectively 0.36 and 0.46 per cent carbon.

The curves of Figure 81 are difference curves of a series of very pure carbon steels taken by Carpenter and Keeling.

The purpose of Rosenhain's derived differential method of plotting is to eliminate the irregularities from which difference curves still suffer and which are due chiefly to differences between the heat capacities and emissivities of the sample and neutral body resulting in differences in their rates of cooling and heating. The resulting curves are obtained by the replotting of the data afforded by the difference (θ vs. $\theta - \theta_1$) curves. Some of Carpenter and Keeling's results replotted by Rosenhain according to his derived differential method are shown in Figure 82. Rosenhain has designed an ingenious instrument permitting the autographic recording of derived differential curves.

The different types of cooling curves described in the preceding pages are well illustrated in Figure 83. These curves were constructed from the data given in the following table, in which each unit in t represents intervals of time of 15 seconds, θ the corresponding temperatures of the sample, and $\theta - \theta_1$ corresponding differences of temperature between the sample and a neutral body cooling under identical conditions. The curve B, representing the cooling curve of a neutral body free from critical transformations, has been added for comparison.

t	θ	$\theta-\theta_1$	t	θ	$\theta-\theta_1$
5	850.0°	8.5°	18	829.0°	11.0°
6	848.0	8.5	19	825.0	8.2
7	844.7	7.5	19.5	823.3	7.3
8	842.0	7.0	20	822.2	6.7
9	839.5	6.3	21	821.7	7.7
10	838.5	7.0	22	821.5	8.5
11	838.2	8.8	23	821.3	9.8
12	838.1	10.2	24	821.1	10.1
13	838.0	12.0	24.5	819.0	9.5
14	837.9	13.6	25	815.0	6.0
15	837.5	15.5	26	813.0	5.0
16	836.0	14.6	27	811.6	4.7
17	833.0	13.0			

Self-Recording Pyrometers. — With the use of neutral bodies self-recording instruments are generally employed. The self-recording may be by means of photographic plates or by some other mechanical devices. The former method calls for the use of mirror galvanometers sending a beam of light upon the photographic plate, while in other autographic recorders needle galvanometers may be used. The relative merits between photographic recorders and other types are summed up by Burgess as follows:

"It is evidently of great advantage to use self-recording apparatus when possible, and it then becomes necessary to choose between the photographic type and the autographic. The latter possesses the advantage that the experimenter may watch any part of the record, and can therefore control the operation and at any moment vary the conditions affecting the experiment; whereas with a photographic recording apparatus, as usually constructed, the observer does not know whether or not the experiment is progressing properly until it is finished and he has developed the sen-

sitive plate. The manipulation by the photographic method is usually also more delicate and time consuming and the adjustment less sure, and the record often requires further graphical interpretation. The autographic method is in general not adapted for interpreting phenomena taking place within an interval of a few seconds, so that for very rapid cooling it is necessary to employ the photographic method. It is possible to construct the photographic recorder so as to obtain a very considerable range of speeds with the same apparatus, while it is difficult and costly to construct an autographic recorder having more than two speeds."

Other Methods for the Determination of the Critical Points. — The spontaneous evolutions or absorptions of heat observed at the critical points are obviously manifestations of transformations taking place within the metal, and it will be seen in the next chapter that many properties of iron and steel undergo at these temperatures sudden and marked changes. It is obvious, therefore, that the determination of the change taking place in any one of these properties in function of the temperature will afford a means of detecting the existence and location of the critical points. The method fully described in the preceding pages, and by far the most generally used, may be termed the "thermal method." Other methods based on the discontinuity in the variation of certain properties occurring at the critical points will now be briefly described.

Metallographic Method for the Determination of the Critical Points. — Howe and A. G. Levy have used, with marked success, a metallographic method for the determination of the critical points, notably of the point A_3. The method for Ac_3 consists in noting the temperature at which the re-absorption of ferrite is found to be complete, and for Ar_3, the temperature at which rejection of ferrite begins. It will be explained in the next chapter why these phenomena correspond to the occurrence of the Ar_3 and Ac_3 points. The samples of hypo-eutectoid steels are first heated to a high temperature (1200 to 1450 deg.) and slowly cooled in the furnace in order to assemble the ferrite into coarse masses. Specimens of this coarsened steel are then heated to various temperatures below and above the supposed position of Ac_3, holding the temperature stationary for from 30 to 60 minutes. The specimens are then quenched and preferably reheated to some 300 or 400 deg. in order to convert the martensite into troostite and thus secure greater contrast between the free ferrite and the matrix into which it is embedded and hence readier distinction of small amounts of free ferrite. These structural changes are explained in following chapters. The Ar_3 point is determined in a similar manner by noting the temperature at which free ferrite first makes its appearance in cooling down. The successive heatings may be 10 deg. apart.

Calorimetric Method. — A. Meuthen (Ferrum, 1912, Vol. X, p. 1) has determined by the vacuum method of Oberhoffer (Bunsen ice calorimeter and electric resistance furnace) the quantities of heat evolved when iron-carbon alloys cool through their critical points, and the method may be used for the determination of these points. The method has also been used by Weiss and Beck, and by Weiss, Picard, and Carrard.

Thermo-Electric Method. — W. Broniewski (Comptes Rendus, 1913, Vol. CLVI, p. 1983) has applied a thermo-electric method to the determination of the critical points which he considers at least equal in accuracy to other methods. It consists in determining the thermo-electro-motive force of the iron or steel in relation to copper. The occurrence of discontinuity in the variations of the electro-motive force indicates the positions of the critical points. With 0.07 per cent carbon the point A_2 was found

at about 730 deg. In pure iron, A_3 occurred at 950 deg. and in steel with 0.07 per cent carbon its position was 850 deg. With more than 0.44 per cent carbon the points A_2 and A_3 were merged with the recalescence point.

Melting-Points Method. — Stead has devised an ingenious method for the determination of the critical points Ar_1 and Ac_1 (Journal Iron and Steel Institute 1913, II,

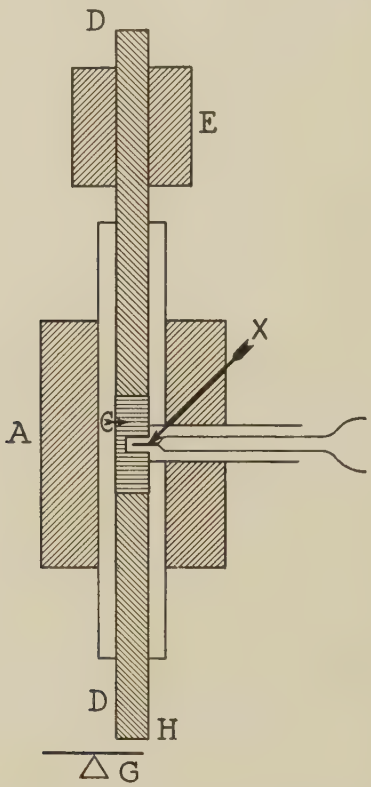


Fig. 84. — Magnetic test for the determination of the thermal critical points in iron and steel.

p. 399) by which the use of pyrometers may be dispensed with, the method being based on the known melting point of sodium chloride and of some metals in the form of wire.

Magnetic Method. — It will be explained in the following chapter that iron-carbon alloys lose their ferro-magnestism, or at least the bulk of it, on heating, in passing through the points Ac_2, $Ac_{3\cdot2}$, or $Ac_{3\cdot2\cdot1}$, as the case may be, and recover it in cooling at the points Ar_2, $Ar_{3\cdot2}$ or $Ar_{3\cdot2\cdot1}$. By observing these magnetic transformations and noting the temperatures at which they occur, the position of these critical points may be accurately determined. The author has found the following procedure very satisfactory. A (Fig. 84) is an electric resistance furnace; DD two round bars of iron (the author uses American ingot iron, a product nearly free from carbon) suitably held in position; C is the piece of iron or steel the magnetic critical points of which are to be determined; X is the hot junction of a thermo-electric couple introduced into a hole drilled in the sample C; E is an electro magnet sur-

rounding a portion of the bar D; G is an iron needle so balanced that it is readily attracted by the end H of the composite bar DCD when the latter is magnetized. As long as the temperature of the piece C remains below its Ac_2 point (or $Ac_{3\cdot2}$, or $Ac_{3\cdot2\cdot1}$ according to the carbon content) the composite bar DCD attracts the needle or keeper G, but when the critical point is reached the magnetic flux ceases to pass

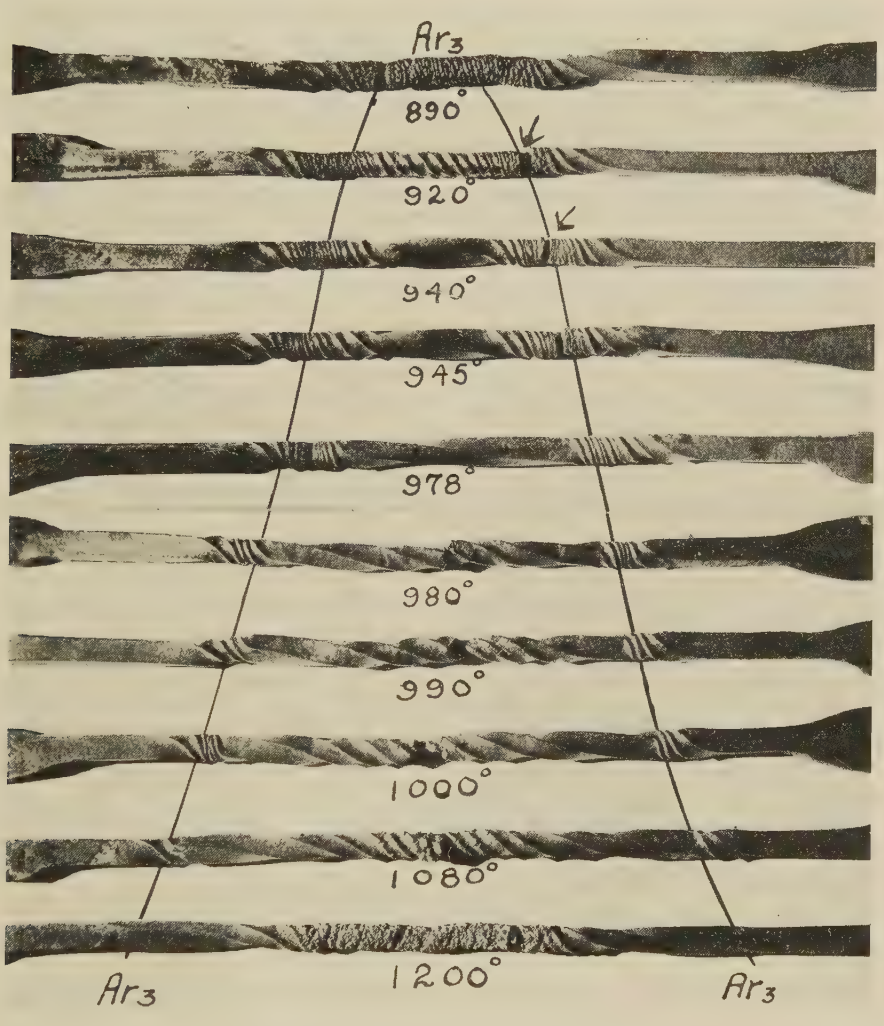


Fig. 85. — Twisting test of electrolytic iron.

through C and the needle drops. The point on heating is in this way sharply recorded. On cooling, as soon as the point Ar_2 is reached, the steel recovers its magnetism and the needle G is again attracted. The method is sufficiently delicate to detect the A_2 point in carbonless iron, and in very low carbon steel.

Dilatation Method. — It will be seen that when iron and steel undergo their critical transformations, sudden dilatations on cooling and sudden contractions on heating are observed, at least at the A_1 and A_3 points. The determination of these abrupt changes

of volume may be used for locating the critical points. The method has been employed by Chevenard with very great success, and the Chevenard dilatometers are widely used.

Twisting Method. — Dr. D. C. Lee and the author have discovered that when iron or steel undergo their A_3 transformation, they become critically plastic. When a bar of iron or of low carbon steel is heated at the center of its length to a temperature exceeding the A_3 point, and then twisted, the twisting does not occur at the center where the bar is hottest, but at two points equidistant from that center where the bar is undergoing its A_3 transformation (Fig. 85). By heating the bar at its center to a lower temperature, although still above A_3, the twists occur nearer the center, and on further decrease of temperature, they finally merge, the bar now twisting at the center. The temperature needed to cause this merging of the twisted portions is that of the A_3 point.

The A_4 Point in Pure Iron. — A thermal critical point which may properly be designated as A_4 has been detected in pure iron by Osmond [1] at 1300° C. Curie,[2] using the magnetic method, also detected it at the same temperature, while Weiss and Föex [3] by the same method observed it at 1395° C. Torajiro Ishiwara [4] has more recently investigated the occurrence of this point, locating it at 1390° C., likewise by the magnetic method.

Honda indicates a temperature of 1400° C. for the Ar_4 point and 1410° C for Ac_4. According to Ruer and Klesper, the point rapidly rises with increase of carbon until for 0.38 per cent carbon it is merged with the melting point of the steel at 1485° C. Its occurrence suggests the existence of iron above the critical temperature of 1390° C. in an allotropic condition, which may be designated as δ (delta).

The A_0 Critical Point. — A reversible magnetic transformation at about 200° C in iron-carbon alloys was first reported by Wologdine, and later studied by Dejean, and by Honda and Tayaki, who place it at 210° C. The existence of this point has been confirmed by others. It is designated by the notation A_0, the symbols Ar_0 and Ac_0 being used to indicate the occurrence of the point respectively on cooling and on heating.

The following table, indicating the location of the critical points in the absence of hysteresis, is from Torajiro Ishiwara:

Transformation	Temperature	Nature
A_0	215° C.	Magnetic transformation of Fe_3C
A_1	727° C.	Eutectic transformation
A_2	800–780° C.	Magnetic transformation of iron and steel
A_3	903° C.	Alpha-gamma transformation
A_4	1390° C.	Gamma-delta transformation

Recapitulation. — Admitting the points A_0 and A_4 in the family, it will be seen (a) that three critical points are observed in carbonless iron, namely, A_4, A_3, and A_2;

[1] Journal Iron and Steel Institute, 1890, I, p. 102.
[2] Œuvres, p. 289.
[3] Archives de Genève, 1911–31, p. 89.
[4] Science Reports of the Tôhoku Imperial University, Vol. VI, No. 3, 1917.

(b) that hypo-eutectoid steels exhibit when containing less than 0.35 per cent carbon, the five points A_4, A_3, A_2, A_1, and A_0, then with increasing carbon, only $A_{3\cdot2}$, A_1, and A_0; (c) that eutectoid steel has two points, $A_{3\cdot2\cdot1}$, and A_0, and (d) that hyper-eutectoid steel has three points, A_{cm}, $A_{3\cdot2\cdot1}$, and A_0.

The A_4, A_3, and A_1 transformations, when cooling or heating are sufficiently slow, complete themselves within narrow ranges of temperature, while the A_0 and A_2 transformations cover an extended range of temperature. In the author's opinion, the claims that A_0 and A_2 merely indicate beginnings or endings of magnetic transformations, and are not therefore to be considered allotropic, should be accepted with reservation.

Historical. — In 1868 Tschernoff in studying the hardening of steel used the notation A for the temperature at which hardening by rapid cooling becomes suddenly possible in high carbon steel. This was the point $Ac_{3\cdot2\cdot1}$.

In 1869 Gore noted that at a dark red heat steel exhibited on cooling a spontaneous dilatation of short duration followed by normal contraction — evidently the point of recalescence Ar_1 or $Ar_{3\cdot2\cdot1}$.

In 1873 Barrett repeated Gore's experiments and discovered, on heating, a momentary contraction at nearly the same temperature as the dilatation on cooling. This was the point Ac_1 or $Ac_{3\cdot2\cdot1}$. He further noted that this dilatation or contraction was very feeble in iron (the A_1 point in very low carbon steel) and very marked in hard steel (the point $A_{3\cdot2\cdot1}$). Barrett also discovered the spontaneous glow taking place on cooling a wire and gave it the name of "recalescence."

In 1879 Barrus showed that the increase of hardness resulting from quenching was not gradual but sudden, thus pointing to the existence of a thermal critical point (the A_1 point).

In 1885 Osmond published his discovery of the upper critical points A_3 and A_2 in iron and low carbon steel and gave the first accurate determination of the position of the point A_1.

CHAPTER VIII

THE THERMAL CRITICAL POINTS OF STEEL

THEIR CAUSES

The thermal critical points described in the preceding chapter are evidently outward manifestations of internal transformations taking place spontaneously at certain critical temperatures. We should now inquire into the nature of these transformations.

Let us remember that there are but three well-known causes of spontaneous evolutions of heat in cooling bodies and of spontaneous absorptions on heating. These are: (1) formation of chemical compounds, a phenomenon which is almost always accompanied by a spontaneous evolution of heat (the heat of formation), and the reverse phase, the dissociation of the compound with absorption of heat (the heat of dissociation), (2) changes of state, that is, the passage of a substance from the solid to the liquid or from the liquid to the gaseous state, or directly from the solid to the gaseous state, which changes are always accompanied by spontaneous absorptions of heat, and the opposite phases of the same phenomena, the passage of a body from the gaseous to the liquid or from the liquid to the solid state, when heat is evolved (the latent heat of solidification in case of a substance passing from the liquid to the solid state, etc.), these evolutions or absorptions of heat, as the case may be, maintaining the temperature of the substance constant while a change of state is in progress, as, for instance, during solidification or melting, (3) allotropic or polymorphic transformations which are always accompanied by an evolution of heat when the body passes from one allotropic condition to another, and by an absorption of heat when it returns to its first allotropic form or vice versa. The meaning of allotropy has been discussed in Chapter III.

Causes of the Upper Points A_3 and A_2 in Carbonless Iron. — It has been seen that at these points spontaneous evolutions or absorptions of heat occur in chemically pure iron which, since they are not accompanied by any change of state (the metal being considerably below its solidification point), must, it seems, necessarily indicate the existence of iron under three allotropic forms. It has been mentioned in Chapter III that the allotropic form stable above A_3 is known as γ (gamma) iron, that stable between A_3 and A_2 as β (beta) iron, and the form stable below A_2 as α (alpha) iron. The following then takes place during the cooling and heating of pure iron: as the metal cools from a high temperature when the point Ar_3 is reached, it passes from the gamma to the beta condition with evolution of heat, while at Ar_2 it passes from the beta to the alpha form also with evolution of heat. On heating the reversals take place, the iron passing with absorption of heat from the alpha to the beta condition at Ac_2 and from the beta to the gamma condition at Ac_3. That the point A_3 indicates an allotropic transformation is universally admitted, no one doubting the

existence of iron in at least two allotropic conditions. Some authoritative writers believe with Osmond that the point A_2 also indicates an allotropic transformation, and that iron, therefore, assumes three distinct allotropic forms, as explained above. While some writers have expressed doubts as to the allotropic character of the point A_2, as will presently be explained, in these pages iron will be assumed to exist in three allotropic conditions, of which A_3 and A_2 are the transformation points, this theory being, in the author's opinion, the one best supported. The possible existence of iron in a fourth allotropic condition, known as δ (delta), above 1390° C., has already been mentioned.

The A_2 Point and Beta Iron. — The arguments which have been offered in support of the contention that the point A_2 of pure iron and of low carbon steel is not an allotropic point and that, consequently, beta iron does not exist, should be briefly considered.

(1) It was claimed by Benedicks and Carpenter that the point A_2, or at least Ac_2, does not occur in strictly pure iron, but in view of the results obtained by Dr. Burgess at the Bureau of Standards, and by others, the claim had to be withdrawn and the existence of A_2 as an independent point is no longer a debatable question.

(2) The point A_2, it has been said, notably by Benedicks and H. Le Chatelier, cannot be an allotropic point because of the absence of hysteresis between the two phases Ac_2 and Ar_2 of the transformation. While it may be that hysteresis has always been observed in allotropic transformations, it does not by any means follow that its absence indicates the non-existence of allotropy. Indeed the freezing and melting of crystalline substances which may be considered as major instances of allotropy occur normally without hysteresis.

(3) The point A_2, we are told, cannot be an allotropic point because no crystallographic change has ever been found to occur at that point. Recent X-ray analyses have shown that beta and alpha iron both have body-centered space lattices. The argument is valid only if it be accepted that an allotropic transformation necessarily implies a crystalline change, a definition of allotropy which is far from being generally entertained. It is quite possible, moreover, that a slight crystallographic change occurs at A_2 which has so far eluded observation.

(4) The absence of dilatation as iron cools through its Ar_2 point reported by some (Charpy and Grenet, and Benedicks) has been claimed to preclude the existence of allotropy. This argument is based on the arbitrary view that an allotropic transformation must necessarily be accompanied by dilatation on cooling and contraction on heating. Some investigators, moreover, believe they have detected a dilatation at Ar_2, while even the results of Benedicks' careful experiments do not conclusively prove the absence of dilatation.

(5) While admitting that a marked transformation takes place at A_2 in the magnetic properties of iron, it has been argued that it was not of an allotropic character (H. Le Chatelier, Weiss, Honda, Benedicks, and others) (*a*) because it was not sufficiently sudden to imply discontinuity, and (*b*) because in general magnetic transformations of that kind are not allotropic. Ac_2, we are told, marks the end of a progressive transformation having its starting point at a considerably lower temperature, while Ar_2 marks the beginning of the reverse change. Starting and end points of progressive transformations, however, are not accompanied by sudden evolution or absorption of heat; slight changes of direction only should occur in the thermal curves. While it is apparently true that the magnetic transformation starts at a temperature

considerably below A_2, the very existence of that point with its notable heat evolution indicates a sharp *discontinuity in the progressiveness* of the transformation and hence suggests allotropy; or, differently expressed, iron on being heated from atmospheric temperature to just below its Ac_2 point loses *progressively* possibly 50 per cent of its ferro-magnetism, while in passing through its Ac_2 point it loses *abruptly* the remaining 50 per cent. It is unjustifiable to describe the phenomenon as merely a progressive transformation.

The recent theories put forward to show that the loss of ferro-magnetism suffered by some metals on being heated should not be regarded as allotropic transformations are purely arbitrary and speculative. It remains more consistent to regard the magnetic and non-magnetic conditions of the same substance as two allotropic states of that substance.

The following, from Professor Honda,[1] is an example of the kind of speculation resorted to in order to explain away the thermal point A_2:

> It remains to explain what is the nature of the progressive change in the A_2 transformation. It is not the change of atomic configuration, as is the case with the allotropic change, but very probably a gradual change of energy in atoms accompanying the rise of temperature. According to the theory of Dr. J. Okubo and the present author, the gradual diminution of magnetisation with rise of temperature is due to the increasing velocity of rotation of the atoms about their magnetic axes. The angular velocity of this rotation is assumed to be comparatively small at room temperature, and the gyrostatic resistance to the turning of the magnetic axes of the atoms in the direction of the field is very small. But as the temperature is continuously increased to a very high degree, the angular velocity, by virtue of thermal impact among atoms, always becomes greater, and hence the gyrostatic action of the atoms rapidly increases, the substance becoming thereby less and less magnetisable, till magnetisation vanishes. Here it is to be assumed that when the field ceases to act, the direction of the magnetic axes takes a distribution uniform in all directions by virtue of thermal impact. Thus in this theory, the A_2 transformation is of the progressive nature and the change will obviously be a definite function of temperature, as actually observed. The heat absorbed during Ac_2 transformation is the energy required to increase the angular velocity of the atoms, while the heat evolved during Ar_2 transformation is the energy of rotation liberated.

(6) It has been contended that no discontinuity in any of the properties of iron has even been proved to take place at A_2 and that, therefore, the transformation cannot be an allotropic one. To this it may be answered (*a*) that the existence of a marked thermal critical point indicates a sharp discontinuity in the internal energy of iron, and that as an evidence of allotropy it is at least as conclusive as a discontinuity in any other property, (*b*) that discontinuity undoubtedly exists at A_2 in the magnetic properties of iron, and (*c*) that several investigators have noted a discontinuity in the dilatation of the metal (Rosenhain and Humfrey), although denied by others, in its tensile strength (Rosenhain and Humfrey), in its specific heat (Weiss and Beck, and Meuthen), and in its electrical resistance (G. K. Burgess and I. N. Kelberg). In regard to the latter property Burgess and Kelberg write:

"The exact determination of the variation of the electrical resistance of pure iron (99.98) in terms of temperature has been made over the range 0 to 950 deg. C., particular attention being given to the form of the curve over the A_2 and A_3 critical ranges. . . . No anomalies are found in the resistance of iron until the A_2 region is approached, and at A_2 there is an inflection at 757 deg. C. in the resistance temperature curve shown as a sharp cusp in the temperature coefficient. At Ac_3 the resistance of iron falls abruptly by some 0.005 of its value, which is recovered within a 25

[1] Journal Iron and Steel Institute, May, 1922.

deg. interval, and above Ac_3 it increases greatly again. On cooling, the Ar_3 is accompanied by slight increases of resistance with falling temperature. Ac_3 and Ar_3 begin at the same temperature, 894 deg. C., and each extends over a temperature interval of 25 degrees. These resistance measurements show that A_2 is a strictly reversible transformation and A_3 is a transformation taking place at a higher temperature on heating than on cooling. These experiments are in agreement with the thermal observations previously recorded in Scientific Paper No. 213.

"Whether or not either or both of these critical ranges A_2 and A_3 are to be considered allotropic points will depend upon the definition of allotropy, about which there does not appear to be agreement."

(7) To explain the existence of A_2 in impure iron without having recourse to allotropy, Benedicks attempted to show, through ingenious speculations, that the point Ar_2 indicated the end of the Ar_3 transformation, some gamma iron remaining untransformed below Ar_3 owing to the presence of impurities, the phenomenon being one of supercooling, and the resulting equilibrium therefore metastable. What had been hitherto called beta iron was in reality, then, a solid solution of gamma iron in alpha iron. As this highly speculative hypothesis demands the absence of A_2 (at least of Ac_2) in strictly pure iron, it may be considered as untenable. Benedicks, however, facing this difficulty, attempted to explain that unless the cooling be very slow the point Ar_2 might still occur in pure iron without disproving his theory, and likewise Ac_2 on quick heating. He admits, however, that the intensity of A_2 should gradually decrease as the purity of the iron increases. The facts are that both Ac_2 and Ar_2 occur sharply in the purest irons obtainable on very slow heating and cooling and that there are no indications of their decreasing in intensity in the purer metals. Benedicks' attempt to replace a theory simple in its conception and well supported by experimental evidences by a product of intellectual gynmastics has failed. Osmond's theory originated and grew in the laboratory, in close harmony with nature, while Benedicks' theory was evolved in the quiet of one's study.

Those who deny the allotropic character of the A_2 point generally claim that their conclusion is not based upon an arbitrary definition of allotropy and then immediately proceed to define allotropy in such a way as to exclude the A_2 transformation.

From the foregoing considerations the following conclusions appear warranted: (1) A_2 is an independent thermal point and is a manifestation of a transformation taking place spontaneously in iron and low carbon steel, (2) A_2 can in no way be regarded as the end point or starting point of the A_3 transformation, and (3) whether A_2 marks or not an allotropic transformation depends on our definition of allotropy. If it be insisted that allotropy necessarily implies a change of crystalline forms, then it may be argued that A_2 is not an allotropic point. If, on the contrary, it is considered that a discontinuity in the internal energy of iron, made evident by spontaneous evolution or absorption of heat, is the criterion by which to judge of allotropy, then we are justified in believing in the existence of beta iron. This view is strengthened by the undoubted existence of a discontinuity in the magnetic properties of iron at the A_2 point, and of discontinuities observed by some investigators in other properties.

Causes of the Upper Critical Points A_3 and A_2 in Low Carbon Steel. — As might be expected, the points A_3 and A_2 occurring in very low carbon steel also indicate allotropic changes in the metal. According to most writers, however, only that portion of the metal which at ordinary temperature exists as free ferrite is here affected.

To make this matter clear it will be necessary to anticipate somewhat our subject, while the diagram shown in Figure 86 will be useful. The possible existence of delta iron between the solidification point and 1390° C. is not indicated in this diagram.

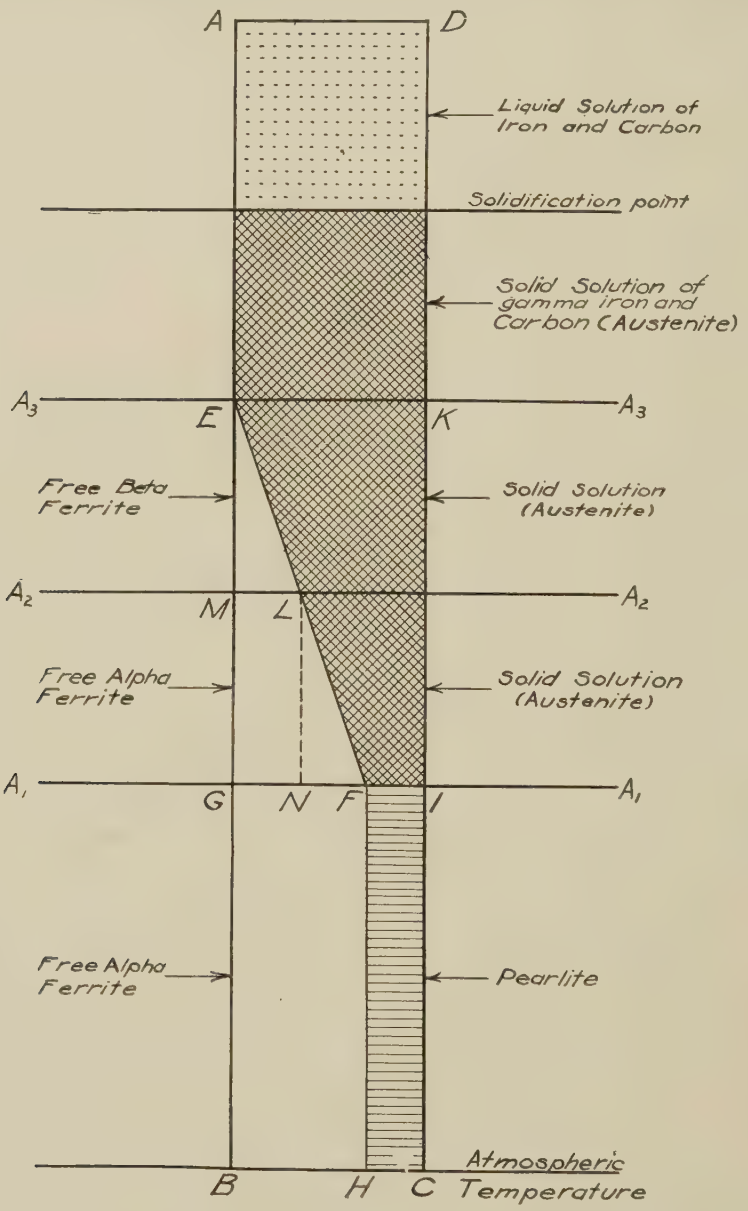


Fig. 86. — Diagram depicting structural changes in 0.20 per cent carbon steel as it cools slowly from the molten condition to atmospheric temperature.

In this diagram the three critical points of steel containing 0.20 per cent carbon, A_3, A_2, and A_1, as well as its solidification point and atmospheric temperature, are represented by parallel lines drawn at suitable intervals in the scale of temperature. The metal is represented by the rectangular area *ABCD*. The diagram illustrates

the following facts later to be discussed at greater length: (1) In the molten condition steel is considered to be a liquid solution of iron and carbon; (2) on reaching its solidification range the metal is converted into a solid solution of gamma iron and carbon known as austenite; (3) upon reaching Ar_3 some ferrite begins to be set free; (4) the ferrite as it is set free assumes the beta state, this liberation of ferrite and its allotropic transformation being probably one and the same phenomenon; (5) the formation of free ferrite continues as the steel cools from Ar_3 to Ar_1, *EFG* representing the ferrite thus liberated; (6) on reaching the point Ar_2 the ferrite liberated between Ar_3 and Ar_2, *ML* in the diagram, passes from the beta to the alpha condition; (7) the ferrite liberated between Ar_2 and Ar_1, *LNF* in the diagram, assumes the alpha condition (according to some writers) without passing by the beta condition, while in the opinion of others the beta condition is assumed but is immediately followed by the alpha state; (8) while ferrite is being set free, the balance of the steel, *EKIF*, (according to most writers) preserves its condition of solid solution, gamma iron plus carbon; (9) upon reaching the point Ar_1 the residual solid solution, *FI*, is converted bodily into pearlite; (10) from Ar_1 down to atmospheric temperature no further structural change takes place, the steel being finally made up of *BH* = *GF* per cent ferrite and of *HC* = *FI* per cent pearlite.

On heating, the opposite changes take place: (1) at Ac_1 transformation of *FI* pearlite into *FI* solid solution (gamma iron + carbon = austenite), while this solid solution begins immediately to assimilate some of the free ferrite, which as it is assimilated passes to the gamma condition; (2) between A_1 and A_3 absorption of free ferrite continues, being completed at Ac_3; (3) on reaching the point Ac_2 the ferrite, *ML* in the diagram, which has not been absorbed between Ac_1 and Ac_2 now passes to the beta condition. This diagram depicts accurately the generally accepted views in regard to the meaning of the critical points. If these views are correct several interesting inferences may be drawn as to the relative intensities of the critical points. The point A_3 in low carbon steel does not indicate a complete transformation, as is too often loosely stated, but merely the *beginning*, at Ar_3, or the *end*, at Ac_3, of a transformation extending over a considerable range of temperature, i.e. from A_1 to A_3. Theoretically, therefore, it would seem as if the point A_3 must correspond to a mere change of direction in cooling and heating curves rather than to well-marked jogs. The fact that a decided jog marks the point Ar_3 in very low carbon steel might be ascribed to hysteresis, the metal cooling to a temperature below that at which the A_3 change is due so that when the transformation begins to take place it does so with added intensity, hence the jog. The jog corresponding to the Ac_3 point of very low carbon steel is not so readily explained. But is not this jog much less pronounced than the one corresponding to Ar_3? The point Ar_2 marks (1) a complete transformation, namely, the passage from the beta to the alpha state of the free ferrite liberated between Ar_3 and Ar_2 and (2) the beginning of a transformation, namely, the passage to the alpha condition of the ferrite which continues to be liberated between Ar_2 and Ar_1. Because of the complete transformation implied by the point A_2 we readily understand that it should correspond to a jog both in the heating and cooling curves, and since Ar_2 is due chiefly to the allotropic transformation of the ferrite liberated between Ar_3 and Ar_2, we readily understand why it should occur at nearly the same temperature regardless of the carbon content. In the light of what precedes, however, the point A_3 in steel instead of being regarded as the manifestation of transformations occurring and completing themselves at a certain temperature, in reality

indicates the *beginning* or *end* of transformations extending over a considerable range of temperature, namely, from A_3 to A_1.

Cause of the Point $A_{3\text{-}2}$. — It has been seen that the point $A_{3\text{-}2}$ is apparently a merging of the points A_3 and A_2 of lower carbon steel and it seems natural to infer

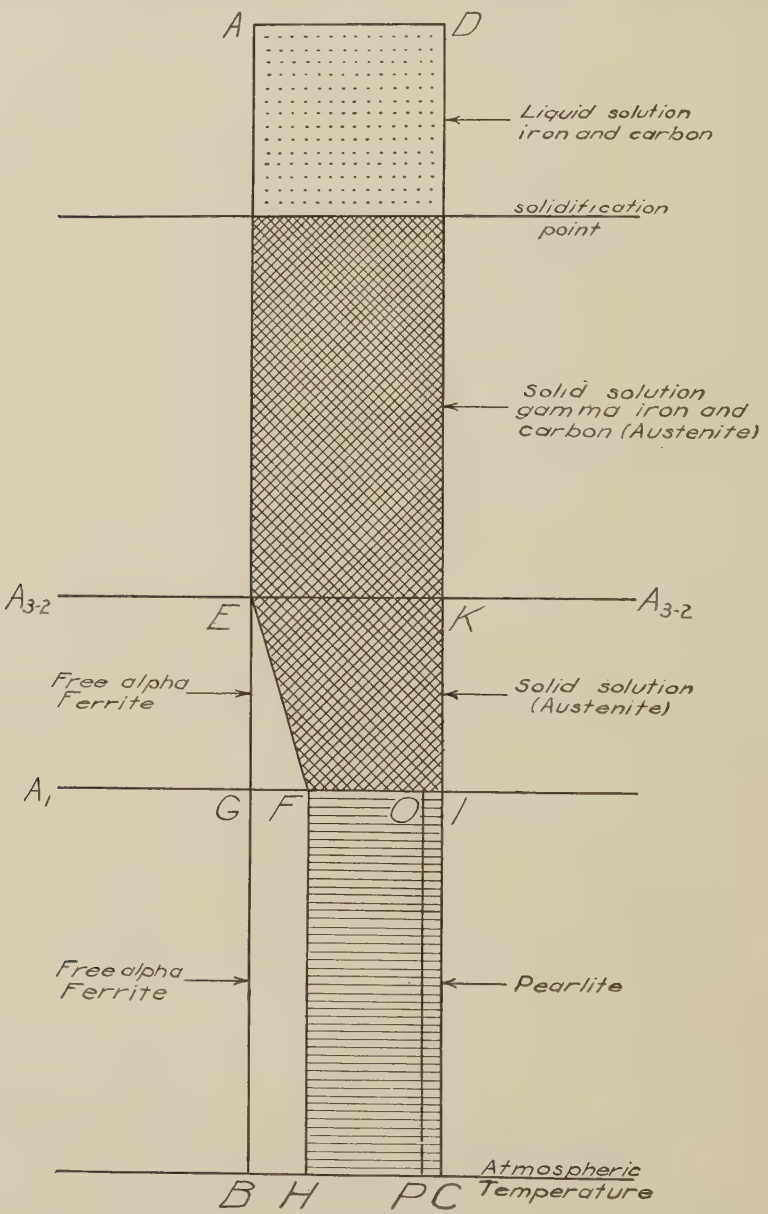


Fig. 87. — Diagram depicting structural changes in 0.60 per cent carbon steel as it cools slowly from the molten condition to atmospheric temperature.

that the transformations which these points indicate, namely the two allotropic changes, are here likewise merged, that is, that they now take place at the same temperature. In other words that when the point $Ar_{3\text{-}2}$ is reached on cooling, the iron

passes from the gamma to the beta and then immediately to the alpha state, the heat evolved being due to this double allotropic transformation. Many now claim, however, that at the point $Ar_{3\cdot2}$ the iron passes directly from the gamma to the alpha condition, the change of gamma to beta being suppressed in steel containing over 0.35 per cent carbon or thereabout, if indeed it ever takes place. If such hypothesis were true it would have some important bearing upon the probable theory of the hardening of steel as explained in another chapter. In these chapters the point $A_{3\cdot2}$ will be considered as implying a double allotropic change. Most metallographists believe that like the independent points A_3 and A_2 the double point $A_{3\cdot2}$ is the result of allotropic changes affecting the free ferrite only.

This setting free and allotropic transformation of ferrite is depicted diagrammatically in Figure 87 in the case of steel containing 0.60 per cent carbon and having, therefore, the two critical points $A_{3\cdot2}$ and A_1. *EGF* indicates the gradual liberation of ferrite and its conversion to the alpha state as the metal cools from $Ar_{3\cdot2}$ to Ar_1, the steel, after complete cooling, being made up of $BH = GF$ per cent ferrite and $HC = FI$ per cent pearlite.

If, as generally stated, the allotropic transformation of which $A_{3\cdot2}$ is a manifestation affects only the free (pro-eutectoid) ferrite, the intensity of the point $A_{3\cdot2}$ must decrease rapidly with decreasing pro-eutectoid ferrite, i.e. as the eutectoid composition is approached, and this point must vanish altogether as it meets the point A_1 (see Chapter VII, Fig. 75), from which it further follows that the single point of eutectoid steel is not in reality a triple point as the notation $A_{3\cdot2\cdot1}$ would imply, resulting from the merging of A_1 and $A_{3\cdot2}$, but that on the contrary it remains a single point, being merely the continuation of the A_1 point of hypo-eutectoid steel.

Cause of the Point A_1. — It has been seen that the point A_1 does not occur in carbonless iron, only feebly in iron containing little carbon, and with increased intensity as the carbon increases to the eutectoid point. The conclusion seems irresistible that the point A_1 must be closely related to the carbon, that it must indicate a sudden change in its condition. If steel be rapidly cooled from above the point Ac_1 and then treated with certain dilute acids, practically all the carbon escapes as hydrocarbons, whereas the same steel after slow cooling through Ar_1 when similarly treated yields a carbonaceous residue, which upon being analyzed is found to consist of the carbide Fe_3C. It is assumed that upon quick cooling we retain the carbon, partially at least, in the form in which it normally exists above A_1, and seeing that when subjected to a similar treatment this carbon behaves so very differently from the carbon of slowly cooled steel, the conclusion is very logical that carbon exists above A_1 in a different condition from that normal below A_1. Above A_1 it is often called "hardening" carbon, below A_1 "cement" carbon. On heating steel past the point Ac_1 the carbon changes from the cement to the hardening condition, and vice versa on cooling at Ar_1 from the hardening to the cement condition. It is, moreover, believed by some that this hardening carbon is carbon in solid solution in the iron. If it be so the heat evolved at Ar_1 is clearly, in part at least, the heat of formation of the carbide Fe_3C and the heat absorbed at Ac_1 clearly the heat of dissociation of that carbide, which now is resolved again into its elements according to the reversible reaction

$$Fe_3C \leftrightarrows 3\ Fe + C$$

The intensity of the A_1 point should then increase as the carbon increases or, rather, as the amount of pearlite increases, and should be maximum, therefore, at

the eutectoid point, as indicated in Figure 75, Chapter VII. With higher carbon content it diminishes slightly because the free (pro-eutectoid) cementite which is now present takes no part in the transformation occurring at Ar_1, having been formed at a higher temperature, namely, between Ar_{cm} and Ar_1, as later explained.

It would seem that the cause of the A_1 point, i.e. the point of recalescence, is in this way explained in a perfectly satisfactory manner. The correctness of this theory appears to be further supported by microscopical evidences which reveal the presence of Fe_3C in slowly cooled steel while pointing to the probable absence of it in suddenly cooled steel.

In recent years, however, it has seemed more and more probable to many students of metallography that it is not carbon in its elementary state which is dissolved in iron at a high temperature, but rather the carbide Fe_3C itself, and that the difference between the behavior of the carbon in hardened steel and in slowly cooled steel might well be satisfactorily accounted for on the ground that in hardened steel Fe_3C is *dissolved* in iron and in that form is much more readily acted upon by acids, being thereby converted into hydrocarbons, whereas Fe_3C when in the free crystallized condition, as in slowly cooled steel, resists the action of the acids and remains undissolved. If it is Fe_3C and not C which is dissolved in iron above the critical range, it is evident that the point Ar_1 cannot be caused by the *formation* of Fe_3C. But it may well be due to the crystallization or falling out of solution of Fe_3C. To be sure this is a falling out of a solid solution, but cannot we conceive that the falling out of a constituent of a solid solution is accompanied by an evolution of heat even if it does not imply a change of state? In other words is it not possible, or even probable, that crystallization in the solid state is accompanied by an evolution of heat? Surely this crystallization implies an allotropic or at least a polymorphic transformation, and are not such transformations always accompanied by heat evolutions?

The author offers these thoughts as possibly worthy of attention and as a possible explanation of the evolution of heat at Ar_1 if we assume that Fe_3C and not C is dissolved in iron above that point.

It should be recorded here that Jeffries and others believe that Fe_3C, and, for that matter, any other metallic compound, could not be dissolved as such in iron because of lack of space between the iron atoms to accommodate molecules. The carbon, they say, must be present in atomic dispersion. While the argument is difficult to refute, it fails to carry conviction.

The Point A_1 an Allotropic Point. — Most writers describe the point A_1 as purely a carbon point, that is a manifestation of a change affecting the condition of the carbon only, as explained in the foregoing pages. These same writers, however, assert that the upper critical points, A_3 and A_2 in low carbon steel, or $A_{3\cdot2}$ in higher carbon steel, affect only the condition of the free (pro-eutectoid) ferrite. In this they are inconsistent, for if the upper point or points indicate allotropic transformation of the free ferrite only, then the lower point A_1 is decidedly an allotropic point seeing that it corresponds to allotropic transformations of the pearlite-ferrite and that in steel containing more than some 0.40 per cent carbon there is more pearlite-ferrite than free ferrite. In other words the point A_1 is always an allotropic point, indicating an allotropic transformation of the pearlite-ferrite similar to the allotropic transformation of the free ferrite occurring at the upper points, and in case of steel with more than 0.40 per cent carbon the allotropic change taking place at A_1 affects a larger bulk of iron than the change at $A_{3\cdot2}$. To make the matter clear let us consider

(Fig. 87) a steel containing some 0.60 per cent of carbon and, therefore, made up after slow cooling of 70 per cent of pearlite and 30 per cent of free ferrite. This steel will contain 61 per cent of pearlite-ferrite represented by *FO*. When the point A_1 is

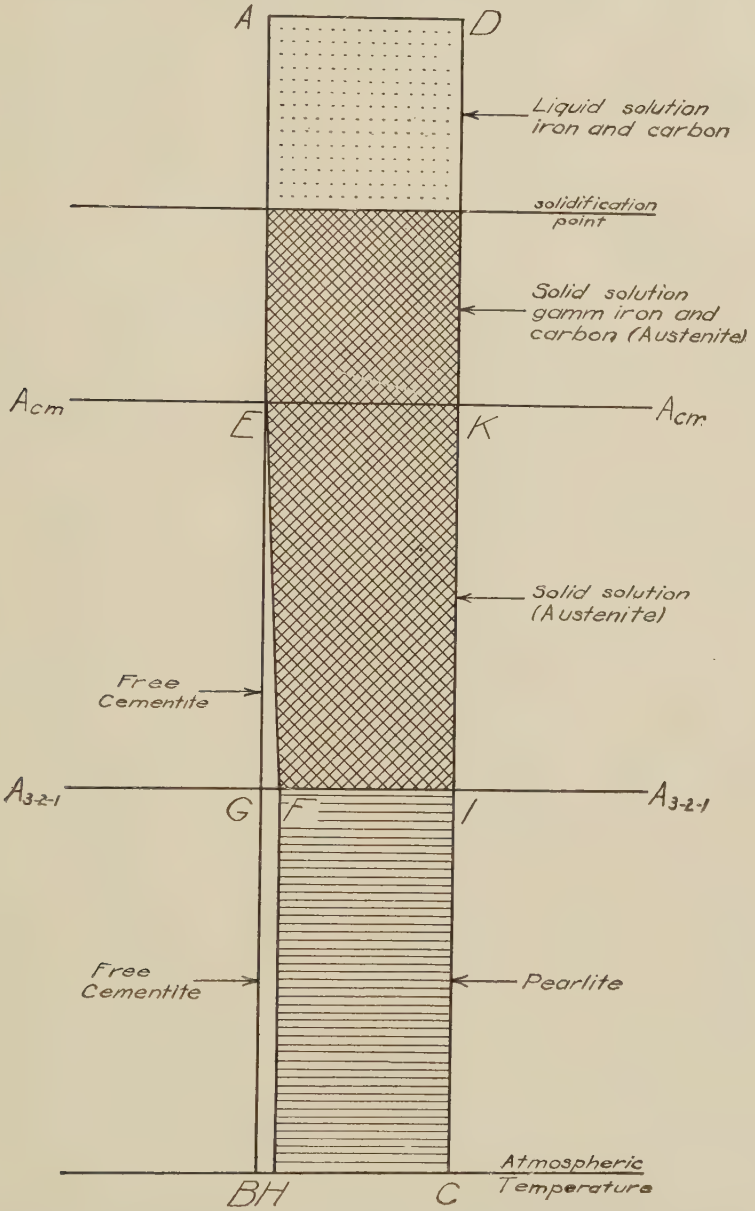


Fig. 88. — Diagram depicting structural changes in 1.25 per cent carbon steel as it cools slowly from the molten condition to atmospheric temperature.

reached this 61 per cent of iron is still in the gamma condition (according to the general belief) and now passes to the alpha condition either directly or first assuming the beta state. The allotropic character of the point A_1 is therefore evident. Indeed it is sufficient to account for the heat evolved at Ar_1 or absorbed at Ac_1 without the

assistance of any change occurring in the carbon condition, for it is in perfect agreement with the increased intensity of the point A_1 as the carbon increases and with its maximum at the eutectoid composition, since as the carbon increases the amount of pearlite and therefore of pearlite-ferrite likewise increases.

Summing up, three reasons may be given for the evolution of heat at Ar_1: (1) formation of the carbide Fe_3C based on the assumption that carbon as such is dissolved in iron, (2) crystallization of the carbide Fe_3C based on the assumption that this carbide is dissolved in iron and that crystallization not implying a change of state may produce heat, and (3) allotropic transformation of the iron present in austenite of eutectoid composition. It seems probable that both (2) and (3) contribute to the heat developed at Ar_1.

Pearlite Formation. — Whatever differences of opinion may exist as to the exact cause or causes of the evolution of heat corresponding to the point Ar_1 all agree that it is due to the transformation of austenite of eutectoid composition (sometimes called hardenite) into pearlite, i.e. the conversion of a solid solution into an aggregate (ferrite plus cementite). It is well to bear in mind the changes in the condition of the iron and carbon which this transformation seems to imply: (1) passage of the iron from the gamma to the beta condition, (2) immediately followed by its conversion into alpha iron or, according to some writers, (1 and 2) the conversion of gamma iron directly into alpha iron, skipping the beta state, (3) the crystallizing of alpha iron into parallel plates or lamellæ, and (4*a*) the formation and crystallizing, or (4*b*) the crystallizing only of Fe_3C into parallel plates alternating with the ferrite plates.

Cause of the Point A_{cm}. — The point Ar_{cm} undoubtedly indicates the beginning of the liberation of free cementite in hyper-eutectoid steel as it cools from Ar_{cm} to $Ar_{3\cdot2\cdot1}$. This gradual formation of free cementite is well shown in Figure 88, where it is represented by the triangle *EFG*. When the point $Ar_{3\cdot2\cdot1}$ is reached the residual austenite, now of eutectoid composition, is converted bodily into pearlite, the steel consisting finally of $BH = GF$ per cent free cementite and $HC = FI$ per cent pearlite. It will be seen that this upper point of hyper-eutectoid steel, like the points A_3 and A_2 of hypo-eutectoid steel, does not indicate a complete transformation but merely the beginning of a transformation covering a wide range of temperature, namely, from A_{cm} to $A_{3\cdot2\cdot1}$. If it corresponds to a jog rather than to a mere change of direction in cooling curves, this must be ascribed to hysteresis and its tendency to accentuate the beginning of a transformation, as previously explained. The evolution of heat corresponding to the liberation of free cementite may be explained in two ways: (1) actual formation of Fe_3C, carbon and not the carbide being in solution above Ar_{cm}, or (2) crystallization or falling out of solution of Fe_3C based on the more probable assumption that Fe_3C and not C is dissolved by the iron above Ar_{cm}, and on the further assumption that this crystallization in the solid state, since it evidently implies an allotropic or, at least, polymorphic change, must be accompanied by an evolution of heat.

Since in hyper-eutectoid steel containing even as much as 1.5 per cent carbon there is but a small proportion of free cementite (some 11 per cent) the point Ar_{cm} is caused by the evolution of but a small amount of heat and must therefore be faint. Its intensity, moreover, must decrease as the carbon decreases and the point must disappear altogether as the eutectoid composition is reached, that is just as it meets the single point of eutectoid steel. This is indicated in Figure 75 of Chapter VII.

Allotropy of Cementite. — If we believe that Fe_3C and not C forms a solid solu-

tion with iron above the point A_1 or $A_{3\cdot2\cdot1}$, it follows that this dissolved Fe_3C crystallizes or falls out of solution at certain critical temperatures, namely Ar_{cm} for the free cementite of hyper-eutectoid steel and Ar_1 (or $Ar_{3\cdot2\cdot1}$) for the pearlite-cementite of all

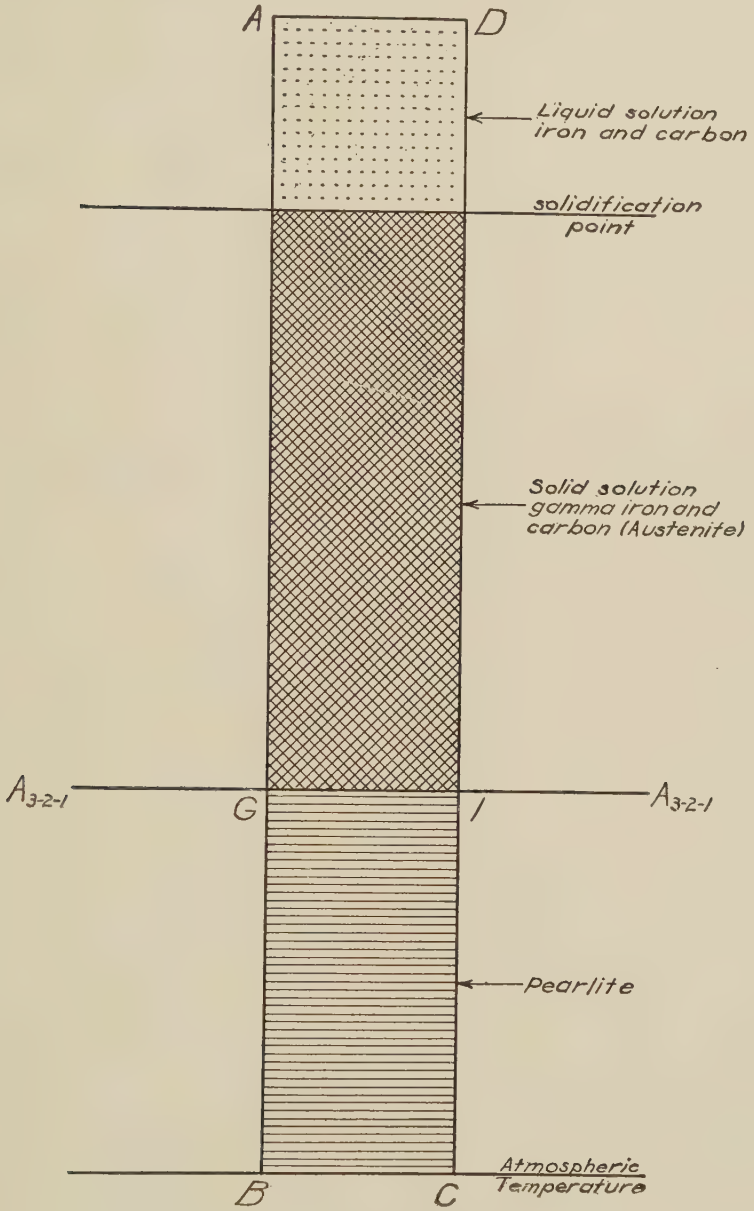


Fig. 89. — Diagram depicting structural changes in eutectoid steel as it cools slowly from the molten condition to atmospheric temperature.

steels, and that this crystallization is accompanied by an evolution of heat. This falling out of solution really implies a spontaneous change of crystalline form and is therefore an evidence of polymorphism, hence of allotropy, for if allotropy does not necessarily imply polymorphism, polymorphism implies allotropy. Are we not then

justified in believing that Fe_3C may exist under two allotropic forms: (1) dissolved in iron, which we may call gamma cementite, and (2) a crystallized variety, which we may call alpha cementite, constituting the free cementite of hyper-eutectoid steel and the hard plates of pearlite.

The fact that the crystallizing or falling out of solution of free ferrite in hypo-eutectoid steel implies an allotropic transformation of the liberated ferrite, points with force to a similar transformation forming part of the liberation of free cementite in hyper-eutectoid steel. In the case of iron we are able actually to prove this allotropy through the cooling of very pure iron and the testing of its properties, while in the case of cementite such direct proof is not yet at hand because of the difficulty of obtaining pure cementite and of testing it after producing it.

To generalize, it would seem as if the crystallizing or falling out of solution of a substance at certain critical temperatures always implies a spontaneous change of crystalline form and, therefore, an allotropic transformation of the substance separating from the solution, whether that solution be liquid or solid. In the former case the falling out of solution implies a change of state, the separating substance passing from the liquid to the solid state, but does it make it less of an allotropic change? Allotropic transformations which also imply changes of state might be called instances of major allotropy to distinguish them from those instances in which changes of internal energy are not accompanied by changes of state.

Cause of the Point $A_{3\cdot2\cdot1}$ in Eutectoid Steel. — In the case of eutectoid steel the solid solution (austenite) is originally of eutectoid composition and, therefore, on cooling reaches the point $Ar_{3\cdot2\cdot1}$ without rejecting either ferrite or cementite, hence the absence of upper points in eutectoid steel. On passing through the point $Ar_{3\cdot2\cdot1}$ (Fig. 89) this austenite is converted into pearlite. Pearlite contains 87.25 per cent of ferrite which undergoes allotropic transformation at $Ar_{3\cdot2\cdot1}$, hence the intense allotropic character of this point. The crystallizing of cementite probably contributes also to the heat evolved at $Ar_{3\cdot2\cdot1}$ whether it implies the *formation* of Fe_3C or not, as explained before. It has also been argued that this crystallizing of cementite probably implies an allotropic transformation, in which case the point $A_{3\cdot2\cdot1}$ (and A_1 as well) would be solely an allotropic point, resulting from the simultaneous allotropic transformation of both the iron and the Fe_3C of austenite of eutectoid composition.

Finally, let us bear in mind that notwithstanding its notation the single point of eutectoid steel does not in fact result from the merging of the several points of hypo-eutectoid steel, being merely a continuation of the point A_1. This point A_1 is essentially a "pearlite" point while the upper points of hypo-eutectoid steel are "ferrite" points and the upper point of hyper-eutectoid steel is a "cementite" point.

Cause of the Point $A_{3\cdot2\cdot1}$ in Hyper-Eutectoid Steel. — The point $A_{3\cdot2\cdot1}$ in hyper-eutectoid steel is of exactly the same nature as the point $A_{3\cdot2\cdot1}$ of eutectoid steel and the point A_1 of hypo-eutectoid steel. It marks the formation of pearlite, bearing in mind the various changes in the condition of the carbon and iron implied by that formation. As the proportion of pearlite now decreases with increase of carbon the intensity of the point $A_{3\cdot2\cdot1}$ likewise diminishes.

Cause of the A_4 Point. — As previously stated, it is believed by some that an allotropic transformation occurs in pure iron in the vicinity of 1400° C., iron above that temperature being in the δ (delta) condition. The addition of carbon causes the transformation to occur at higher temperatures, until with some 0.35 per cent carbon it reaches the melting point of the metal, and therefore disappears. If these views

are correct, it necessarily follows that carbonless iron solidifies as delta iron, steel containing less than some 0.35 per cent carbon as a solid solution of carbon in delta iron, and steel containing more carbon as a solid solution of that element in gamma iron.

The atomic configuration of delta iron has not yet been positively determined by X-ray analysis because of the difficulty of operating at such high temperature. Honda believes, however, judging from its physical properties, that the space lattice of delta iron must be body-centered like that of alpha iron.

Cause of the A_0 Point. — The point A_0 corresponds to the magnetic transformation of cementite (Fe_3C) and resembles, therefore, the point A_2 marking the magnetic transformation of iron. In both cases the transformation covers a wide range of temperature, the point Ac_0, it is claimed, corresponding to the end of the transformation on heating, and Ar_0 to the beginning of the reverse transformation on cooling. Like the point A_2, the point A_0 is almost exactly reversible, that is Ar_0 and Ac_0 occur at exactly or nearly the same temperatures. Those, therefore, who do not believe in the allotropic character of the A_2 transformation likewise deny that the A_0 change is an allotropic one. The arguments offered in support of the contention that A_2 indicates an allotropic transformation of iron may be applied with the same force in support of the view that A_0 indicates an allotropic transformation of cementite. They will not be repeated here. A marked discontinuity in the electric resistance of steel has also been reported at the point A_0. As should be expected, the magnitude of the A_0 transformation increases with the carbon content, and is nil in carbonless iron.

The evolution of heat occurring at A_0 is apparently too slight to permit the detection of that point by thermal analysis.

Summary. — The apparent cause of the thermal critical points of iron and steel may be briefly summed up as follows:

The point Ar_4, assuming its existence in iron and in steel containing less than some 0.35 per cent carbon, indicates the passage of iron from its delta to its gamma condition, or the transformation of a solid solution of carbon in delta iron into a solid solution of carbon in gamma iron.

The point Ar_3 of carbonless iron and of steel containing less than some 0.35 per cent carbon marks the beginning of the liberation of ferrite (which liberation continues down to the point Ar_1) and the transformation of that ferrite from the gamma to the beta (or alpha) condition, this setting free of ferrite and its allotropic transformation being probably simultaneous.

The point Ar_2 of carbonless iron and of steel containing less than some 0.35 per cent carbon indicates the transformation from the beta to the alpha condition of the ferrite liberated between Ar_3 and Ar_2 and the beginning of the passage of the ferrite, which continues to be liberated as the metal cools from Ar_2 to Ar_1, from the gamma to the beta and then to the alpha condition, or, as some writers claim, directly from the gamma to the alpha state.

The point $Ar_{3\cdot2}$ of steel containing somewhere between 0.35 and 0.85 per cent carbon marks the beginning of the liberation of ferrite, which takes place between $Ar_{3\cdot2}$ and Ar_1, and the passage of that ferrite from the gamma to the beta condition and immediately to the alpha state, or, according to some writers, directly from the gamma to the alpha condition.

Since only the formation and transformation of free ferrite is involved at the points A_3, A_2, and $A_{3\cdot2}$, these points may properly be called "ferrite" points.

The point A_1 of hypo-eutectoid steel, as well as the point $A_{3\cdot2\cdot1}$ of eutectoid and hyper-eutectoid steel, marks the rather sudden transformation of the residual solid solution (austenite), now of eutectoid composition, into pearlite, bearing in mind the changes in the conditions of the iron and carbon which such transformation implies. The points A_1 and $A_{3\cdot2\cdot1}$ may properly be called "pearlite" points.

The Ar_0 point, assuming its existence in all iron-carbon alloys, and accepting the claims of many, corresponds to the beginning of the transformation of cementite from a para-magnetic to a ferro-magnetic condition.

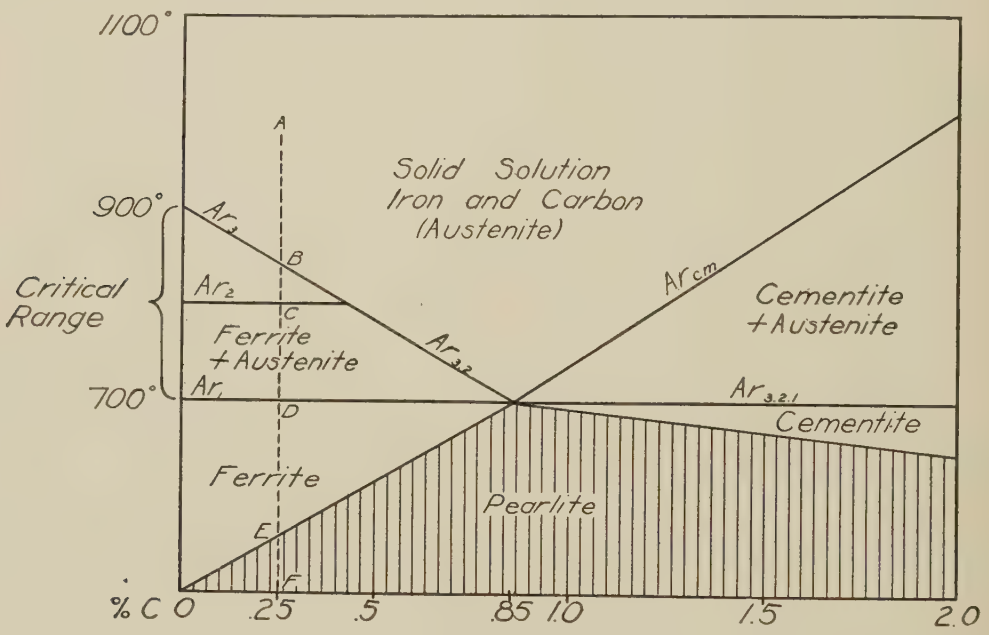


Fig. 90. — Diagram showing the relation between the critical points and the structural composition of slowly cooled steel.

The point Ar_{cm} of hyper-eutectoid steel marks the beginning of the setting free of cementite as the metal cools from Ar_{cm} to $Ar_{3\cdot2\cdot1}$, the liberation of cementite probably involving an allotropic change of that constituent, as previously explained.

In Figure 90 an attempt has been made at showing diagrammatically the relation between the critical points of steel and its structural composition after slow cooling, the points A_4 and A_0 being omitted. It will be readily understood. The upper part of the diagram shows the location of the critical points, the lower part the structural composition in percentages of ferrite, pearlite, and cementite. Taking, for instance, a steel containing 0.25 per cent carbon: above A_3 at A it is a solid solution of carbon and iron (austenite); on cooling through Ar_3 at B some beta ferrite is set free, this liberation continuing from B to C; on cooling through Ar_2 at C the free beta ferrite is converted into alpha ferrite, while additional alpha ferrite forms as the metal cools to Ar_1, that is from C to D. The ferrite liberated on cooling from B to D, that is on cooling through the critical range, is represented in the lower part of the diagram by DE, which is also the final precentage of free ferrite in the steel. As the metal cools through its Ar_1 point at D, the residual austenite, at present of eutec-

toid composition, is converted into pearlite, *EF* representing the pearlite here formed, i.e. the percentage of pearlite in the steel. The structural formation of any steel

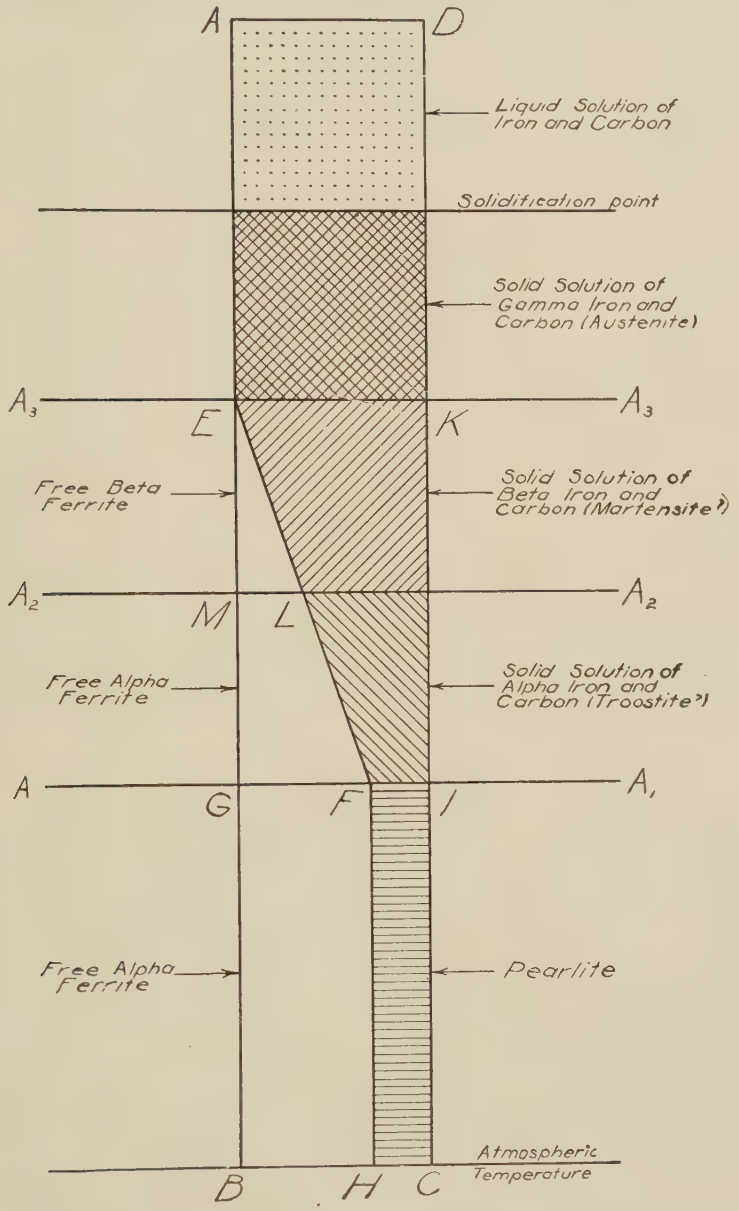


Fig. 91. — Diagram depicting structural changes in 0.20 per cent carbon steel slowly cooled, assuming that the iron remaining in solution as well as the free iron (ferrite) undergoes allotropic changes. To be compared with Figure 86.

can be followed in the same way in this diagram. It will be obvious that the vertical distances representing the percentages of ferrite, pearlite, or cementite in any steel may also be regarded as proportional to the intensities of the corresponding critical

points. For instance, the distance *ED* may be assumed to be proportional to the combined intensities of the points Ar_3 and Ar_2 of a 0.25 per cent carbon steel and the distance *EF* proportional to the intensity of the A_1 point. Interpreted in this way the diagram indicates what has already been pointed out: (1) that the intensities of A_3 and A_2 decrease as the carbon increases, these points vanishing on reaching the eutectoid composition, (2) that the point A_1, very faint at first, increases rapidly with increased carbon, becoming maximum at the eutectoid point and then decreasing, and (3) that the point A_{cm}, always faint, increases slightly as the carbon increases above 0.85 per cent.

Another View of the Allotropic Changes.[1] — It will be obvious from the description of the underlying causes of the critical points given in the foregoing pages that, according to the general belief, iron must first be freed from solid solution before it can undergo any allotropic changes or, at least, its liberation from solution and its allotropic transformation take place simultaneously, the latter never preceding the former. In 1906 the author expressed the opinion that it was far from certain that its liberation from solution must precede, or at least be simultaneous with, the allotropic changes affecting iron at certain critical temperatures. He ventured to put forward, in a tentative way, the hypothesis that iron in solution might first undergo an allotropic transformation and then be expelled in its new allotropic form. This view was not favorably received but, as it has not been shown to be by any means untenable, the author still believes it worthy of record in these pages. It is evident that if the allotropic transformation of iron from the gamma to the beta and then to the alpha state precedes its liberation from solution, three solid solutions of carbon in iron are formed during the slow cooling of steel, namely, carbon (or the carbide Fe_3C) dissolved (1) in gamma iron, (2) in beta iron, and (3) in alpha iron. The first solid solution is universally called austenite, while the hypothesis leads almost irresistibly to regarding the solid solution in beta iron as martensite and the solid solution in alpha iron as troostite, two constituents to be described later.

With the assistance of the diagram, Figure 91, and by comparing it with Figure 86 the working of the present hypothesis will be readily understood. In Figure 91 are depicted the structural changes taking place during the slow cooling of steel containing 0.20 per cent carbon and therefore exhibiting the three critical points A_3, A_2, and A_1. On cooling through the point A_3 the solid solution of carbon and gamma iron (austenite) existing above A_3 is converted into a solid solution of carbon in beta iron (martensite?). In the beta condition, however, iron cannot be retained in solution and begins immediately to be liberated, and its liberation continues as the metal cools down to A_2. Between A_3 and A_2 we have a solid solution of beta iron decreasing in amount and increasing free beta ferrite. On cooling through Ar_2 both the free beta ferrite and the dissolved beta ferrite pass to the alpha state, giving rise to the formation of free alpha ferrite and of a solution of carbon in alpha iron (troostite?). On cooling from Ar_2 to Ar_1 additional alpha ferrite is liberated, while the proportion of carbon-alpha iron solution decreases correspondingly. At Ar_1 the remaining solution has become of eutectoid composition and is converted bodily into pearlite, the mechanism of this transformation being well understood. It will be evident that in the case of hypo-eutectoid steel having but one upper critical point, $Ar_{3\cdot2}$, in cooling through that point the metal would pass from the condition of a solid solution of carbon in gamma iron to that of a solid solution in beta iron and then immediately to that of a solid solution in alpha iron, the steel between $Ar_{3\cdot2}$ and Ar_1 being composed of this solution in alpha iron (troostite?) and of free alpha ferrite. With eutectoid steel the following changes would take place as it cools through its single critical point $Ar_{3\cdot2\cdot1}$: (1) transformation of gamma iron solid solution (austenite) into beta iron solid solution (martensite?), (2) immediately followed by the formation of alpha iron solid solution (troostite?), (3) immediately followed by formation of pearlite.

The author thinks that the decreasing intensities of the points A_3 and A_2 as the carbon content increases is the fact most difficult to reconcile with the hypothesis just outlined, for if these points

[1] These speculations, dating back some twenty years, in regard to the possible meaning of the thermal critical points which the author still considers justified, have been criticized by some and the author accused of insisting upon their correctness. The reader will note that, on the contrary, he offers them with becoming modesty. As the arguments presented by his critics do not in his opinion diminish their plausibility, they are again inserted in the present edition.

are due to allotropic transformations affecting the entire bulk of the steel their intensities should be quite independent of the amount of carbon present. To be sure, this gradual diminution of the magnitude of the points A_3 and A_2 as the carbon increases is likewise difficult of explanation in the light of the universally accepted hypothesis that free iron only can be allotropically transformed, for

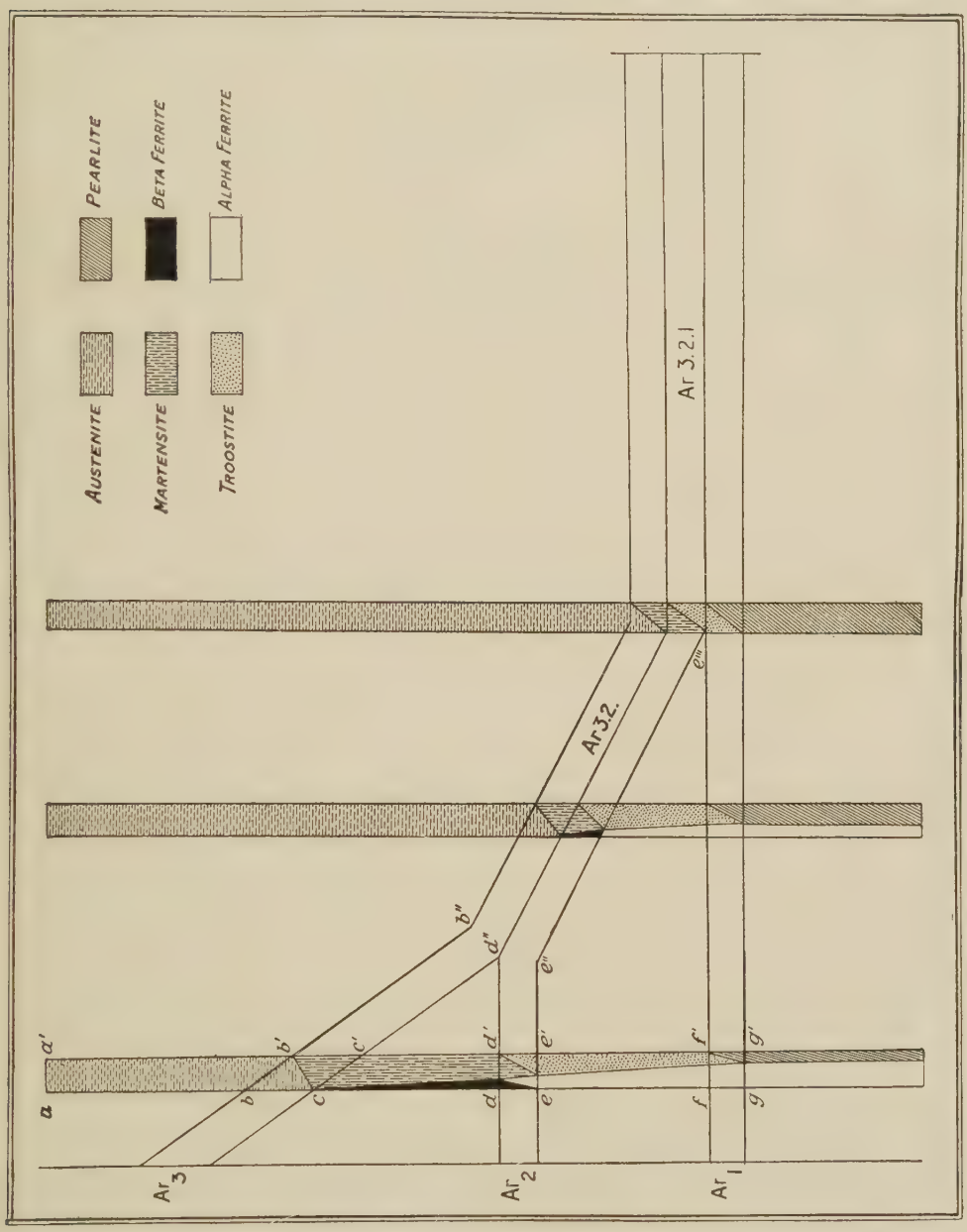


Fig. 92.

it has been made clear in the foregoing pages that these points must indicate then the *beginnings* of transformations and not transformations carried to completion at those critical points, so that the intensities of the points should be little affected by the magnitude of the transformations themselves, that is by the amount of free ferrite undergoing allotropic transformation or, which is the same thing, by the percentage of carbon in the steel.

The view just outlined as to the mechanisms of the allotropic changes is further depicted diagrammatically in Figure 92, in which the critical points are represented as covering certain ranges of temperature making it possible to show, graphically, the changes taking place within these ranges. Taking an iron-carbon alloy having, for instance, the composition *a* (some 0.20 per cent carbon), the diagram shows that above Ar_3 it is made up of *aa'*, i.e. of 100 per cent austenite; on cooling through Ar_3 it is gradually converted into martensite; between Ar_3 and Ar_2 beta ferrite is liberated; in passing through Ar_2 the remaining martensite is gradually converted into a solid solution of carbon and alpha iron (troostite?) while the free beta ferrite is converted into free alpha ferrite; between Ar_2 and Ar_1 additional alpha ferrite is liberated; in cooling through Ar_1 the remaining solid solution (troostite?), now of eutectoid composition, is converted into pearlite. The structural changes occurring in steel having but one upper critical point and in steel of eutectoid composition are similarly depicted.

The reader, after noting the author's view on the hardening phenomenon as expressed in Chapter XVI, when he attributes to martensite and troostite constitutions different from those outlined here, may accuse him rightly of inconsistency. His defense is a confession of ignorance as to positive knowledge and his desire to avoid dogmatism. Some soundness of argumentation is all he claims for his views.

CHAPTER IX

THE THERMAL CRITICAL POINTS OF IRON AND STEEL

THEIR EFFECTS

It has been shown in preceding chapters that the thermal critical points of iron and steel are due chiefly if not wholly to allotropic transformations of the iron, and possibly of the carbide Fe_3C. It is a well-known fact that when a substance undergoes an allotropic transformation many of its properties undergo likewise deep and sudden changes at the critical temperatures. Color, crystallization, dilatation, conductivity both for heat and electricity, strength, ductility, hardness, specific heat, specific gravity, are properties frequently affected as a body passes from one allotropic form to another. We should expect, therefore, such changes to take place as iron undergoes its allotropic transformations, if not in all, at least in some of the above properties. And it is because such changes do take place that a clear understanding of the occurrence and significance of the critical points is of much practical importance to the iron and steel metallurgist.

Changes at A_4

At the Ar_4 point, which is reported to occur in iron, and in steel containing less than some 0.35 per cent carbon, the iron passes from the delta to the gamma condition, while, according to some, the structure of the crystals changes from the body-centered to the face-centered arrangement. The opposite transformation takes place on heating at the Ac_4 point. It is claimed that discontinuities in some physical properties have been observed at this point.

Honda describes as follows the occurrence and significance of the A_4 transformation:

> Above the A_2 point, the intensity of magnetization is not absolutely zero, and can be measured, if we use a specially sensitive apparatus, such as a torsion-balance . . . at the A_3 point, the magnetization discontinuously decreases and afterwards remains nearly constant. At 1410° C. the magnetization increases discontinuously and afterwards gradually decreases. This discontinuous increase of magnetization shows also another transformation in iron; for here, other properties also change discontinuously. This change is called the A_4 transformation, and the iron above the A_4 point, delta-iron. By X-ray analysis it is shown that delta-iron has again a body-centered cubic lattice; the A_4 transformation during heating then consists of the change of atomic configuration from the face-centered cubic lattice to the body-centered, that is, from gamma-iron back again to alpha-iron. That this should occur at the A_4 point was predicted by the present writer from the change of physical properties at high temperature, such as from the magnetization-temperature curve.
>
> Formerly, four modifications of iron, that is alpha, beta, gamma, delta, were assumed, but at the present time beta-iron is to be excluded as an independent phase and delta-iron is the same phase as alpha-iron. Hence, the four modifications are now reduced to only two, alpha and gamma

irons, or atomistically expressed, to the body-centered and the face-centered cubic lattice, there being no other atomic configurations.

It is not out of place to remark that the tensile strength of pure iron discontinuously increases at the A_4 point, that is, in passing from the body-centered cubic lattice to the face-centered cubic lattice. This is easily conceivable, since the distribution of iron atoms in the face-centered cubic lattice is the closest packed, and the atomic force very rapidly increases with decreasing distance, by a given deformation of the lattice; the atomic force developed to resist this deformation will be much greater in the case of the face-centered distribution of the atoms, than in that of the body-centered distribution.

Changes at A_3

It has been shown that the point A_3 occurs in carbonless iron and in steel containing less than some 0.35 per cent of carbon, and that it is universally believed that this point indicates an allotropic change, the iron passing from the gamma to the

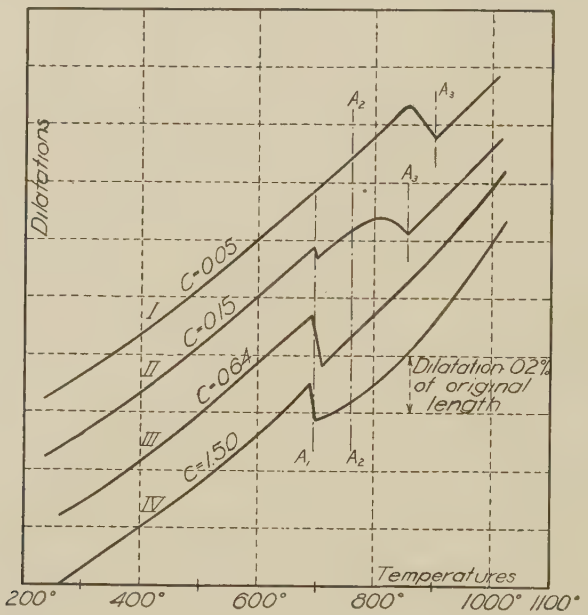


Fig. 93. — Dilatation curves of various carbon steels.

beta condition, or according to some to the alpha condition, on cooling at Ar_3, and vice versa, from the beta (or alpha) to the gamma condition on heating at Ac_3. It should be borne in mind, however, as fully explained in Chapter VIII, that the general belief is that only free ferrite undergoes this change. As the metal cools past its point Ar_3 the following abrupt changes in some of its properties have been noted.

Dilatation. — The metal, which above the point Ar_3 was contracting, as is the general rule with all cooling bodies, on passing through the point Ar_3 undergoes suddenly a marked dilatation, amounting to over $\frac{1}{1000}$ of its length, immediately followed again by a normal contraction. Such dilatation implies that the change of gamma into beta iron takes place with augmentation of volume, or in other words that gamma iron is denser, has a higher specific gravity than beta iron. The dilatations occurring at Ar_3 in the case of steels containing respectively 0.05 and 0.15 per cent carbon are shown graphically in Figure 93. On heating, at Ac_3 a spontaneous

contraction occurs of the same magnitude as the dilatation on cooling. Benedicks determined with great care the dilatation of pure iron between 700 and 950 deg. C. and some of his results are shown in Figure 94. The sharp occurrence of a marked

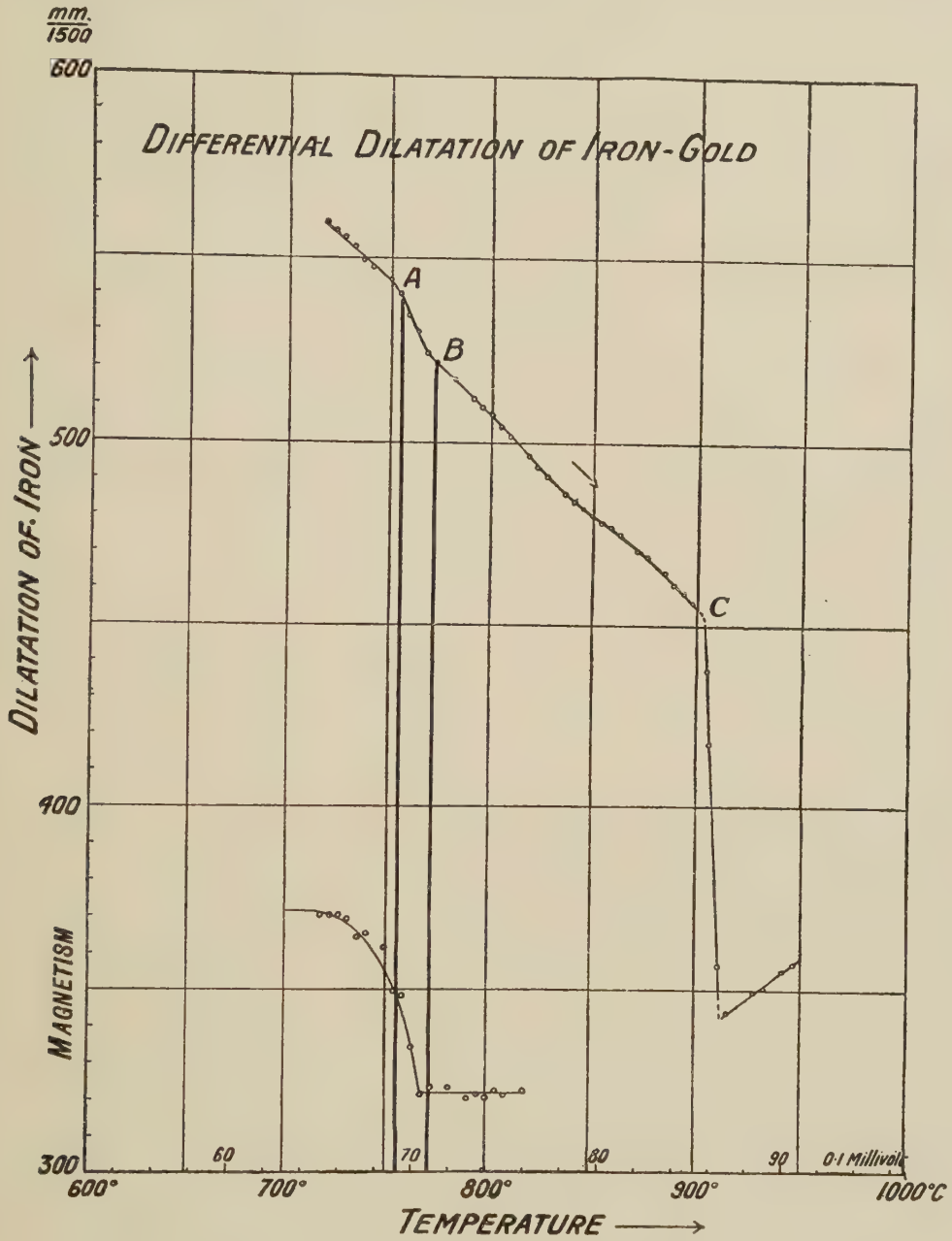


Fig. 94. — Dilatation of pure iron. (Benedicks.)

dilatation at C, the A_3 point, will be noted. Had we no other evidence of an allotropic transformation at this critical temperature, this sudden dilatation taking place as it does in pure iron would justify our belief in its existence.

Electrical Conductivity. — Above the point A_3 the metal has an electrical resistance some ten times greater than its resistance at ordinary temperature. As it cools from a high temperature to the point Ar_3 there is but a feeble decrease of its electrical resistance, but as soon as Ar_3 is reached it begins abruptly and sharply to decrease and keeps on decreasing at a normal rate to atmospheric temperature. At A_3, therefore, we have a sudden and marked change in the variation of the electrical conductivity corresponding to a sharp break in the curve expressing the relation between temperature and electrical resistance as shown in Figure 95. On heating, at Ac_3 the opposite change takes place, that is, the electrical resistance quite suddenly ceases to increase. So marked and sudden a change in a physical property is in itself a proof of an allotropic transformation.

Crystallization. — It has been shown in Chapter III that while gamma and beta iron both crystallize in the cubic system (Osmond), octahedra are the prevailing form

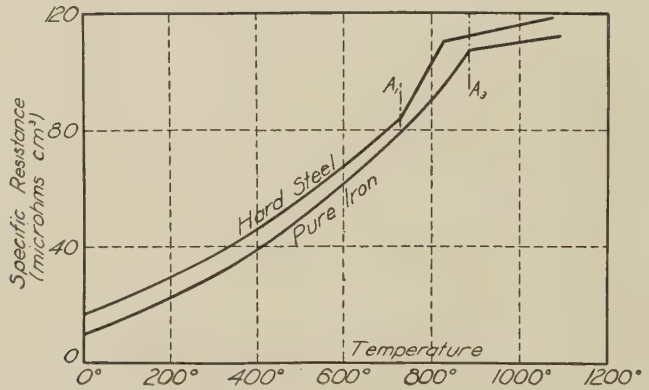


Fig. 95. — Electrical resistance curves of iron and high carbon steel.

of gamma iron while the cube is the crystalline form of beta iron, and that the transformation of gamma into beta iron includes a change in the planes of symmetry, at least of carburized iron (Osmond). According to the results of X-ray analysis, on cooling through A_3 the space lattice of the crystals changes from the face-centered to the body-centered type.

Dissolving Power for Carbon. — Above the point A_3 iron possesses dissolving power for carbon, while according to some writers it loses that power on passing through Ar_3. Non-gamma iron, according to them, cannot dissolve carbon. Admitting the existence of beta iron, however, it does not seem by any means proven that it cannot dissolve carbon. This question is discussed at greater length elsewhere.

Structural Properties. — It has been explained at length in Chapter VII that the point Ar_3 corresponds to an abrupt structural change, namely, the beginning of the setting free of ferrite (Fig. 86, Chapter VII).

Other Properties. — Le Chatelier mentions a change in the variation of the thermo-electric force and a sudden but slight variation in magnetic properties as taking place at A_3. Burgess states that the separate existence of A_3 and A_2 is confirmed by the thermo-electric characteristics of iron. Meuthen reports a discontinuity in the specific heat of iron between 880 and 900 deg. C., that is at the A_3 point.

Plasticity. — The critical plasticity occurring during the A_3 transformation has already been mentioned.

Changes at A_2

As a separate point A_2 occurs in carbonless iron and in steel containing less than some 0.35 per cent of carbon. The changes of properties taking place at A_2 are not generally so abrupt nor are they so marked as those occurring at the other critical points. It is precisely because of this lack of sharpness and suddenness that some have questioned the accuracy of the view that this point, like A_3, indicates an allotropic transformation. Careful consideration of the evidences at hand appear to show, however, that changes of properties do occur at A_2 sufficiently marked and sudden to warrant the classification of this point as an allotropic one. The fact that these changes are more gradual than at the other critical points is logically explained by Osmond on the ground that beta and alpha iron are isomorphous, that is, capable

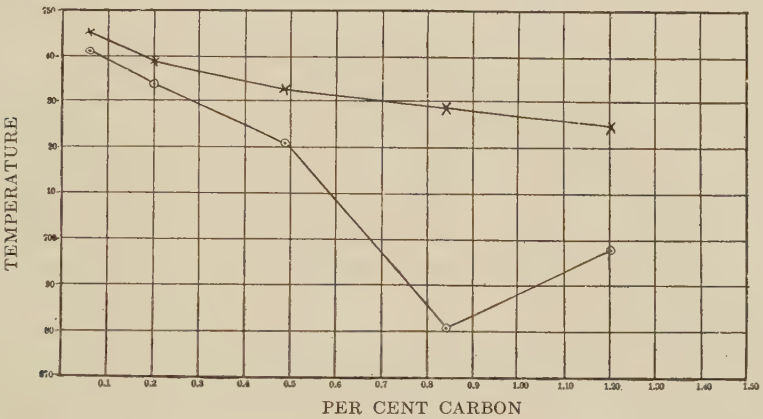


Fig. 96. — Temperatures of magnetic transformations of various carbon steels.

of forming solid solutions, and that therefore the passage of one variety into the other must necessarily be gradual as well as the variations of the properties of iron which the transformation implies.

Dilatation. — According to Le Chatelier, to Charpy and Grenet, to Benedicks and others, no dilatation takes place as the metal cools past the point Ar_2 and they see in this an indication that A_2 is not an allotropic point. Osmond's reply is that the curves obtained by Charpy and Grenet, for instance, do indicate a dilatation at Ar_2 which, however, the authors fail to notice because the transformation not being sudden the dilatation likewise is gradual, whereas the authors were looking for sudden dilatations only. Some of Benedicks' careful measurements of the dilatation of pure iron are shown graphically in Figure 94. The contraction observed on heating, between *A* and *B*, that is during the A_2 range, is described by him as a "slight, fully continuously occurring contraction (under heating) which entirely coincides with the gradual disappearance of the ferro-magnetism." Considering, however, that the striction which clearly reveals the position of A_2 covers a range of temperature not exceeding some 15 deg., it seems to point to a discontinuity in the dilatation of the metal rather than to a perfectly progressive transformation.

Magnetic Properties. — Above the point A_2 steel is non-magnetic, but in passing through Ar_2 it quite suddenly becomes strongly magnetic. Or, to use physicists' terms,

above A_2 iron is para-magnetic, below A_2 it is ferro-magnetic. Is not this momentous change alone, in the magnetic properties of a metal, sufficient proof of an allotropic transformation? It is true that magnetism is not *fully* regained until a considerably lower temperature is reached, probably some 550 deg. C., according to Osmond, but the fact remains that the *greatest part* of the final magnetism of the metal is *abruptly* acquired as it cools past the point A_2. What transformation other than an allotropic one can satisfactorily account for this?

The relation between the carbon content of steel and the temperatures at which the metal loses its magnetism on heating and regains it on cooling is shown graphically in Figure 96. The points plotted in this diagram represent the average values of a great number of determinations made by Madame Sklodowska Curie with a series of very pure carbon steels. It will be noticed that the points of magnetic changes correspond closely to the thermal critical points A_2, $A_{3\cdot2}$, or $A_{3\cdot2\cdot1}$. With little carbon there is but a small gap between the appearance of magnetism on cooling and its disappearance on heating, because the points Ar_2 and Ac_2 occur at nearly the same temperature; with 0.50 per cent carbon the magnetic points are lowered and so, likewise, the point $A_{3\cdot2}$, while the gap increases, this being consistent with the greater gap between $Ar_{3\cdot2}$ and $Ac_{3\cdot2}$; with 0.84 per cent carbon the magnetic points are further lowered and the gap between them increased still more, this being in harmony with the location of the point $A_{3\cdot2\cdot1}$, which is lower than $A_{3\cdot2}$, and with the greater gap between $Ar_{3\cdot2\cdot1}$ and $Ac_{3\cdot2\cdot1}$.

Further experimental evidences that the points of magnetic transformations coincide with the thermal critical points are given in the tables on the following page showing the results of several hundred determinations. All the steels used in connection with the results given in Table II contained in the vicinity of one per cent carbon.

A magnetic method for the determination of the A_2, $A_{3\cdot2}$, or $A_{3\cdot2\cdot1}$ points has been described in Chapter VII.

Crystallization. — The cube being the crystalline form both of beta and of alpha iron and these two allotropic varieties being capable of dissolving each other in all proportions (Osmond), a crystalline transformation at the point A_2 is not to be expected. The crystallography of iron so far as it has been investigated does not reveal the existence of the point A_2. It has already been stated that according to X-ray analysis both beta and alpha iron have body-centered cubic lattices.

Tensile Strength. — Rosenhain and Humfrey have shown the existence of a distinct discontinuity in the tensile strength of iron at the A_2 point.

Dissolving Power for Carbon. — It seems probable that alpha iron does not possess any dissolving power for carbon, or at least that it is only capable of dissolving a very small amount of that element. On the other hand, as already mentioned, it is far from certain that beta iron is incapable of dissolving carbon, statements to the contrary notwithstanding. It is possible, therefore, that on cooling through Ar_2, iron loses its dissolving power for carbon.

Structural Properties. — By referring to Figure 86 of Chapter VIII it will be seen that there is no apparent structural change connected with the point A_2. As the steel cools past Ar_2 the liberation of ferrite started at Ar_3 merely continues, to end only at Ar_1. Of course the ferrite liberated above Ar_2 now passes from the beta to the alpha condition, but this allotropic transformation does not appear to include any structural change.

Specific Heat. — Weiss and Beck, and also Meuthen, have shown that a sharp discontinuity occurred in the specific heat of iron at the A_2 point.

TABLE I. — COMPARISON OF THE MAGNETIC METHOD WITH THE ORDINARY OR COOLING-CURVE METHOD (BOYLSTON.)

Approximate Carbon Content of Steel	Method	$Ac_{3.2.1}$ Mean	$Ac_{3.2.1}$ Max. Min.	Number of Tests	$Ar_{3.2.1}$ Mean	$Ar_{3.2.1}$ Max. Min.	Number of Tests
1.25%	Magnetic	773	788 / 759	7	708	711 / 706	7
	Ordinary	764	781 / 754	4	718	736 / 701	4
		$Ac_{3.2}$			$Ar_{3.2}$		
0.40%	Magnetic	780	790 / 770	7	741	750 / 734	7
	Ordinary	827	830 / 822	3	754	756 / 753	3
		Ac_2			Ar_2		
0.15%	Magnetic	764	772 / 755	6	764	771 / 758	7
	Ordinary	768	772 / 764	2	767	783 / 748	3

TABLE II. — RESULTS OBTAINED BY STUDENTS AT HARVARD UNIVERSITY

Steel Number	Method	$Ac_{3.2.1}$	Number of Tests	$Ar_{3.2.1}$	Number of Tests
1	Magnetic	753	72	679	75
	Ordinary	739	14	688	12
2	Magnetic	752	131	695	136
	Ordinary	750	13	695	17
3	Magnetic	761	55	704	55
	Ordinary	757	55	708	55
4	Magnetic	762	50	700	50
	Ordinary	751	45	701	45
5	Magnetic	776	40	720	40
	Ordinary	760	30	727	30

Changes at $A_{3.2}$

It has been shown that the point $A_{3.2}$ resulting from the merging of A_3 and A_2 occurs, theoretically at least, in steels containing from some 0.35 to 0.85 per cent carbon. As might be expected the changes of properties corresponding to the point $A_{3.2}$ are the same as those taking place in lower carbon steel at A_3 and A_2. As the metal cools through $Ar_{3.2}$ the following variations of properties are, therefore, noted: (1) a marked dilatation, (2) a sudden decrease of electrical resistance, (3) a gain of

magnetism, (4) a discontinuity in the variation of the tensile strength and of the specific heat, (5) a probable loss of dissolving power for carbon, (6) the beginning of the liberation of alpha ferrite (see Chapter VII, Fig. 87).

Changes at A_1

The point A_1 occurs in steel containing from a mere trace to 0.85 per cent carbon. It corresponds, as explained in Chapter VII, to the transformation of the residual austenite (now of eutectoid composition) into pearlite. This formation of pearlite implies that the iron contained in this residual austenite (and forming about 85 per cent of its bulk) undergoes on cooling through Ar_1 the same allotropic changes as those affecting the free ferrite on cooling through Ar_3 and Ar_2 (or $Ar_{3\text{-}2}$). It follows from this that, theoretically at least, the following sudden changes of properties should be noted on cooling through Ar_1: (1) a dilatation increasing with the carbon content and being maximum with 0.85 per cent carbon caused by the allotropic transformation of the iron, (2) increased magnetism because of the transformation of additional non-magnetic gamma iron into magnetic alpha iron, (3) decreased electrical resistance because of additional transformation of high resistance gamma iron into low resistance alpha iron, and (4) additional loss of dissolving power for carbon because of the formation of additional alpha iron.

The point A_1 is not generally associated with critical variations of the electrical and magnetic properties of steel, but on purely theoretical ground it does not seem possible to avoid the conclusion that such critical variations must exist, provided, of course, that we are right in assuming that in austenite of eutectoid composition the iron is still in the gamma condition, that is non-magnetic and of high electrical resistance. Recent investigations have indeed shown that A_1 is distinctly a magnetic point.

Changes at $A_{3\text{-}2\text{-}1}$

The point $A_{3\text{-}2\text{-}1}$ occurs in eutectoid and in hyper-eutectoid steel and marks the transformation of the austenite or eutectoid steel, or of the residual austenite of hyper-eutectoid steel, into pearlite, as shown in Figures 88 and 89, Chapter VII. In these steels, however, no liberation of free ferrite occurs above the point $Ar_{3\text{-}2\text{-}1}$, from which it follows that the *totality* of the iron undergoes its allotropic change or changes on passing through $Ar_{3\text{-}2\text{-}1}$. The variations of the properties which in hypo-eutectoid steel occur at A_3, A_2, and A_1, must therefore, in the case of eutectoid and hyper-eutectoid steel, all take place at the point $A_{3\text{-}2\text{-}1}$. These sudden changes of properties are, on cooling: (1) a marked dilatation, maximum in eutectoid steel (Fig. 93), (2) a sudden decrease of electrical resistance, (3) a sudden gain of magnetism, (4) a loss of dissolving power for carbon.

Le Chatelier mentions the fact that on cooling through Ar_1, or $Ar_{3\text{-}2\text{-}1}$, steel acquires a temporary malleability. If a steel bar, for instance, of sufficient length be held horizontally by one extremity while cooling, it at first remains rigid, but on passing through its point of recalescence it quite suddenly bends. According to Howe this phenomenon was first observed by Coffin.

Structural Change at A_1 and $A_{3\text{-}2\text{-}1}$. — The spontaneous transformation of austenite of eutectoid composition into pearlite, that is of a solid solution into an aggregate, at Ar_1 or $Ar_{3\text{-}2\text{-}1}$, and the reverse transformation, from aggregate to solid

solution, at Ac_1 or $Ac_{3\cdot2\cdot1}$, imply structural changes of momentous importance to the steel metallurgist. While these will be dealt with at length in another chapter it seems proper to record here their significance. These structural changes give the key to the rational treatment of steel. They make possible the refining of steel by heat treatment, seeing that on heating steel through its critical range we may change

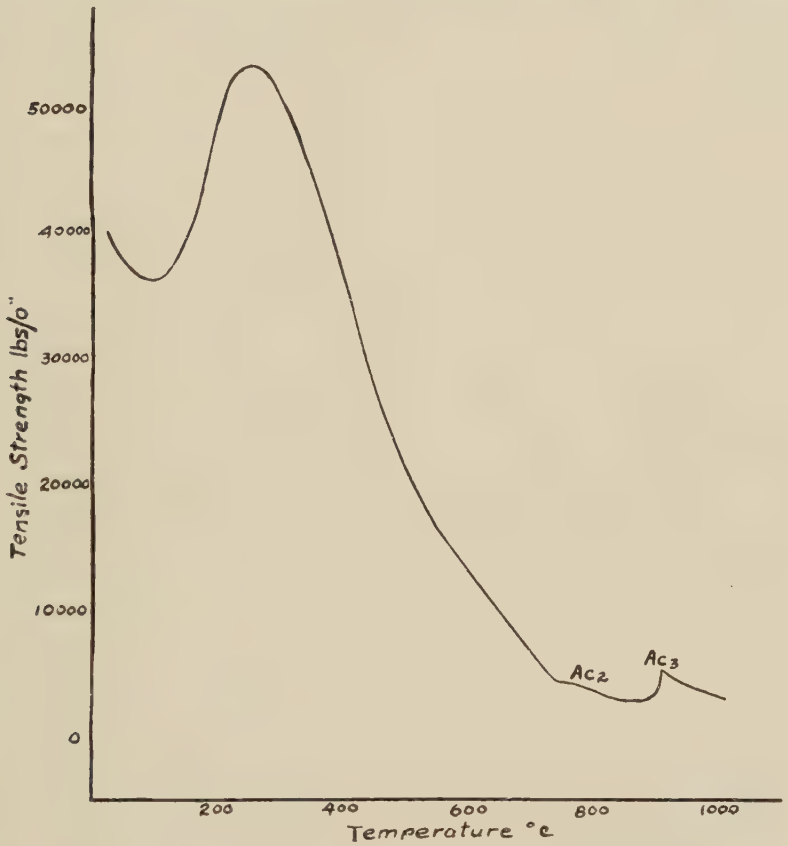


Fig. 97. — Tensile strength vs. temperature of electrolytic iron.

it from the condition of a coarse aggregate (a coarse structure) to the condition of a fine, nearly amorphous, solid solution. They also make possible the hardening of steel through sudden cooling from above the critical range, as will be fully explained in another chapter.

Changes at A_0

It is claimed that as the alloy cools past its A_0 point, the cementite which it contains becomes ferro-magnetic. Honda writes:

> This is the transformation characteristic of cementite; it is in its nature the same transformation as the A_2 transformation in iron. The transformation is progressive and extends from the lowest temperature to 215° C., the change being a definite function of temperature. During heating or cooling, the transformation terminates or commences at the same temperature (215° C.), the A_0 point. This point is observable for all alloys containing free cementite, and has always the same value.

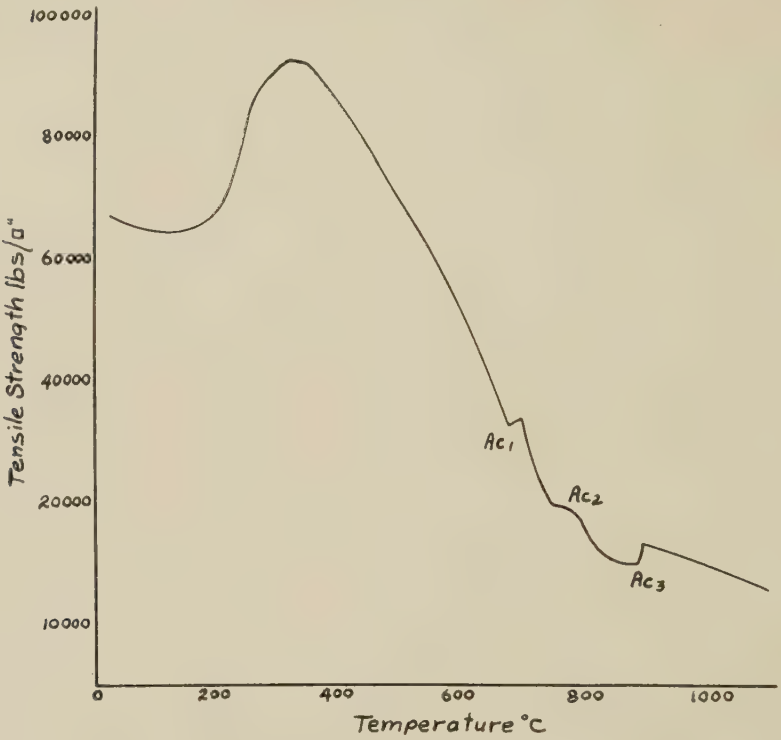


Fig. 98. — Tensile strength vs. temperature of steel containing 0.10 per cent carbon.

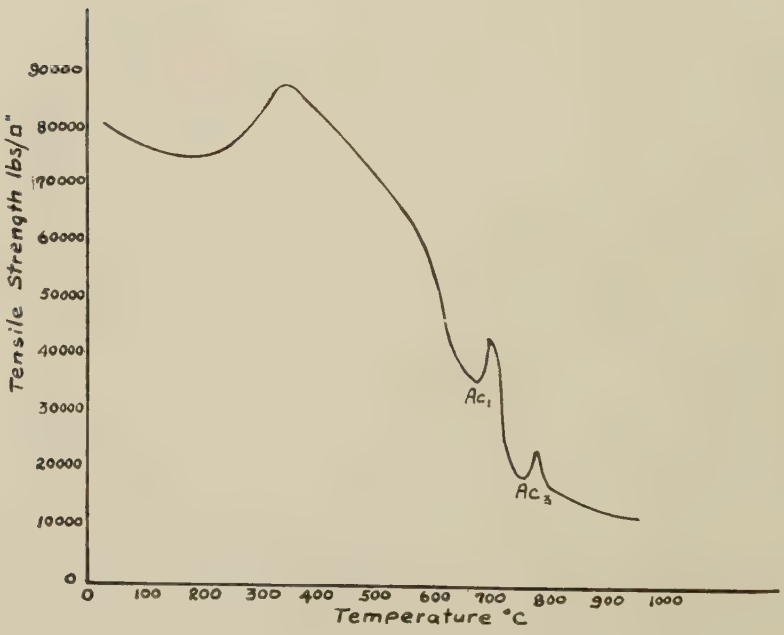


Fig. 99. — Tensile strength vs. temperature of steel containing 0.20 per cent carbon.

Changes at A_{cm}

The point Ar_{cm} occurs in hyper-eutectoid steel and marks the beginning of the liberation of free cementite as the metal cools from Ar_{cm} to $Ar_{3\cdot2\cdot1}$ (see Fig. 88, Chapter VII). Except for this structural change no other marked changes of properties have so far been connected with this point.

Tensile Strength vs. Thermal Critical Points. — Dr. D. C. Lee, in the author's laboratory, has clearly brought out the existence of critical points in the tensile

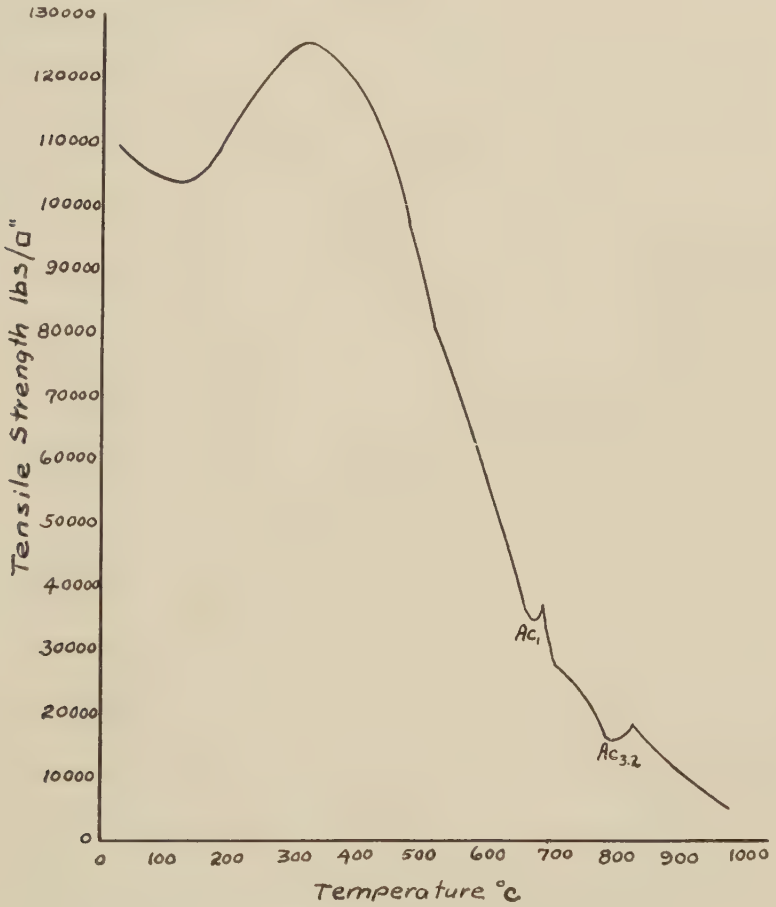


Fig. 100. — Tensile strength vs. temperature of steel containing 0.50 per cent carbon.

strength-temperature curves of iron carbon alloys corresponding to the thermal critical points of these alloys, including the A_2 point, as will be seen by an inspection of Figures 97 to 101. Similar critical points occur in the Brinell hardness-temperature curves.

Rosenhain and Humfrey had previously reported the existence of discontinuities in the tensile strength of steel containing 0.10 per cent carbon, very marked at the Ar_3 point and slight at the Ar_2 and Ar_1 points (Fig. 102).

Prevailing Conditions Above and Below the Critical Range. — The following condensed statement of some of the most significant conditions prevailing above and below the critical range of iron-carbon alloys may be useful in keeping these fundamental facts in mind. By critical range is meant here the critical points, omitting the A_4 and A_0 points, considered collectively, and it will be understood that the

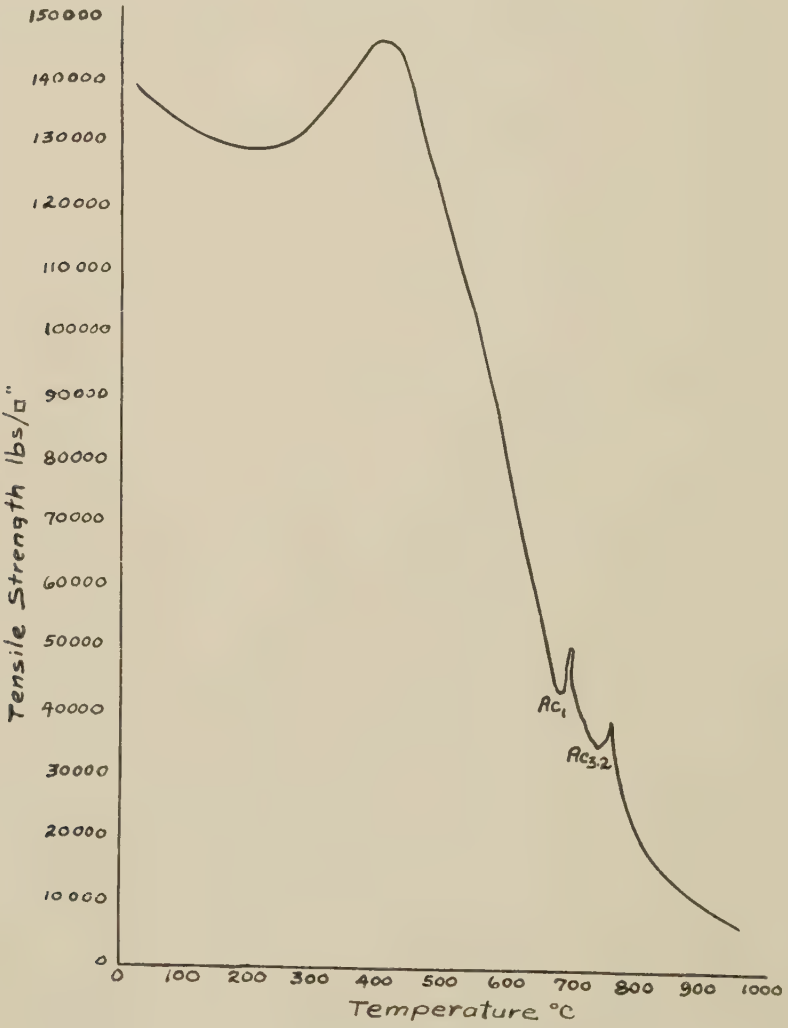


Fig. 101. — Tensile strength vs. temperature of steel containing 0.75 per cent carbon.

conditions described as existing above the range change quite abruptly to the conditions prevailing below the range as the metal cools through the range, or vice versa as it is heated above it. The references made to the crystallizing of the metal, and to the influence of work both above and below the range, will be understood after reading the following chapters dealing with the treatment of steel.

CONDITIONS AND PROPERTIES OF IRON-CARBON ALLOYS AND OF THEIR CONSTITUENTS

Above Critical Range	*Below Critical Range*
Solid solution (austenite).	Aggregate (ferrite + cementite).
Hardening (dissolved) carbon.	Cement carbon (Fe_3C).
Gamma iron.	Alpha iron.
Alloys containing a sufficient amount of carbon possess hardening power.	Same alloys deprived of any hardening power.
Alloys are non-magnetic.	Alloys are magnetic.
Metal crystallizes on slow cooling.	Metal does not crystallize on slow cooling.
Work prevents crystallization.	Work distorts structure.

Properties of Gamma, Beta, and Alpha Iron. — The various properties of gamma, beta, and alpha iron described in the preceding pages have been tabulated on page 142,

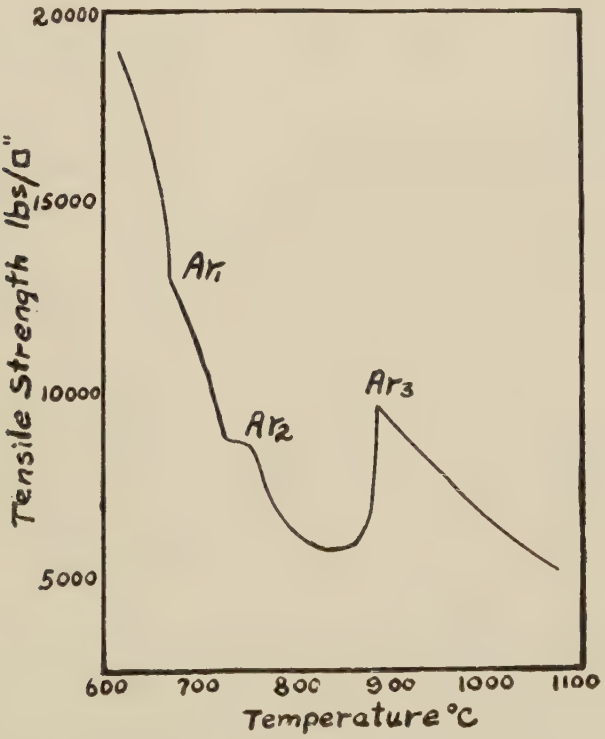


Fig. 102. — Tensile strength vs. temperature in steel containing 0.10 per cent carbon. (Rosenhain and Humfrey).

as well as some other data of interest. These are in accordance with the views held by many, but the author is well aware that those entertaining different views may take exception to some of the entries. It should be remembered that many doubt the existence of beta iron.

	Gamma Iron	Beta Iron	Alpha Iron
Metallurgical name	Austenite	Beta ferrite	Ferrite, alpha ferrite, pearlite ferrite
Solvent power for C (or Fe_3C)	dissolves carbon up to 1.7 per cent or Fe_3C up to 25.5 per cent	probably some but opinions differ	substantially none
Range of temperature in which stable	above A_3, $A_{3\cdot2}$, or $A_{3\cdot2\cdot1}$ in case of pro-eutectoid ferrite, above A_1 or $A_{3\cdot2\cdot1}$ in case of eutectoid ferrite	as free beta ferrite between A_3 and A_2	below A_2, $A_{3\cdot2}$, or $A_{3\cdot2\cdot1}$
System of crystallization	cubic (orthorhombic according to Le Chatelier)	cubic	cubic
Prevailing crystalline forms	octahedra	cubes	cubes
Space lattice	face-centered	body-centered	body-centered
Other crystalline characteristics	frequent twinnings	no twinnings	no twinnings
Specific gravity	greater than beta and alpha iron (dilatation at Ar_3)	greater than alpha iron (gradual dilatation at Ar_2, Osmond)	smaller than gamma and beta iron
Electric conductivity	ten times smaller than that of alpha iron at ordinary temperature	greater than that of gamma iron and increasing with falling temperature	greater than that of beta iron and increasing with falling temperature
Magnetic properties	non-magnetic	feebly magnetic	strongly magnetic
Hardness	softer than beta iron, harder than alpha iron	very hard (?)	soft

CHAPTER X

CAST STEEL

The structural and other changes taking place at the thermal critical points of steel account for the deep changes of properties resulting from the treatments to which steel is subjected in the process of manufacture of finished articles. We are now in a position to understand these changes, to anticipate them, and to arrive at the rationale of the treatment of steel which for so many centuries remained purely empirical.

It is logical that we should first consider the structure of steel before it has received any treatment whatsoever, namely, the structure of the metal in its cast condition. To this study the present chapter will be devoted.

The structure of cast steel is different from what, in these chapters, has been termed the normal structure of the metal because, having been developed during

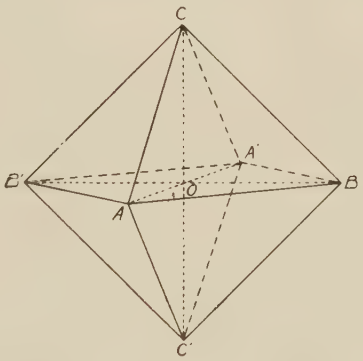


Fig. 103. — Regular octahedron.

very slow and undisturbed cooling from the molten condition, crystalline growth has been promoted, whereas in working and reheating such large growth is hindered or corrected. It may well be expected, then, that the structure of steel castings will be coarser, as is generally expressed, that is made up of larger crystalline grains, than the normal structure so far considered, and therefore that steel castings will suffer from all the ills that pertain to a coarse structure, namely, weakness, lack of ductility, or even brittleness, etc. It will be profitable to consider first the crystallization of steel in general and then the genesis of the structure of cast eutectoid, hypo-eutectoid, and hyper-eutectoid steel.

The greater part of this description is taken from a paper by the author ("Crystallization of Iron and its Alloys") published in the Transactions of the American Society for Steel Treating, July, 1923.

A tiny drop of liquid iron or of steel should, on solidifying, if it obeyed only the laws of crystallography, be converted into a regular octahedron (Fig. 103). As previously stated, such perfect crystals with faultless geometrical outlines are called idiomorphic crystals. The octahedron is a form belonging to the cubic or regular (isometric) system of crystallization. Iron and steel, like most metals, crystallize in the cubic system. The octahedron, therefore, appears to be the crystalline form of both

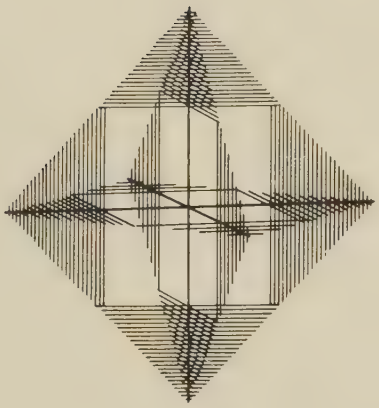


Fig. 104. — Gradual growth of octahedral crystals. From Belaiew's "Crystallization of Metals." (After Knop.)

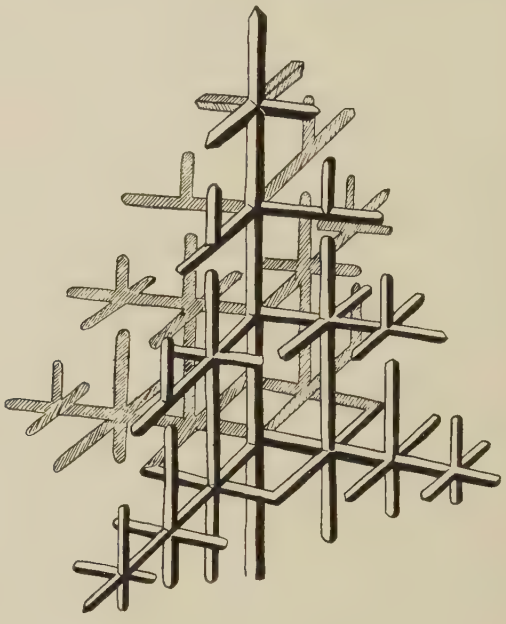


Fig. 105. — Skeleton of octahedral crystals. (After Tschernoff.)

delta and gamma iron. The gradual growth of octahedral crystals has been studied and it has been observed that the main axes are formed first, and that this is followed in quick succession by the appearance of secondary and ternary axes and finally by the filling up of the interstices between the axes (Fig. 104). If the liquid could be removed before this filling up takes place, we would obtain what is sometimes described as skeleton crystals (Fig. 105).

Crystals grow through the successive addition of small crystalline units symmetrically arranged according to the system of crystallization to which they belong. If these units are cubic their corresponding faces will lie in parallel planes. This is called the orientation of the crystals and constancy of orientation is a property of all crystals. As already mentioned, because of this crystalline orientation, crystals possess direction of easy rupture known as cleavage planes. Constancy of crystalline orientation imparts also unlike properties in different directions, that is causes anisotropy. In the case of the octahedron one may, following Howe, conceive the crystalline units to be cubic (Fig. 106). Such octahedral crystal would then have three planes of cleavage parallel to one of the three pairs of faces of the small cubes and four planes parallel to one of the four pairs of faces of the octahedron.

A tiny drop of liquid iron or of liquid steel will not, however, assume, on solidifying, the external form of an octahedron because of contact with the support on which it is solidifying, and of other factors opposing the crystallographic forces. It does crystallize, however, and the mechanism of its crystallization is that of the octahedron. Lacking the external geometrical form of perfect idiomorphic crystals, but retaining a true crystalline structure, they are called allotriomorphic crystals.

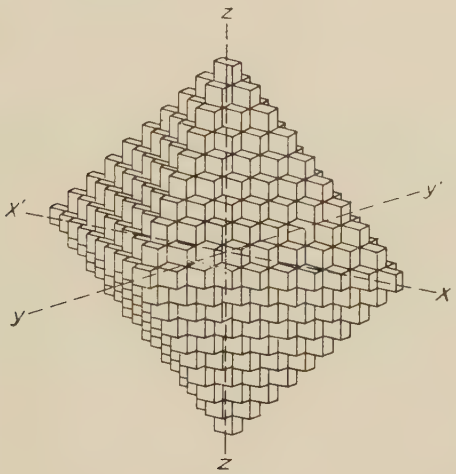


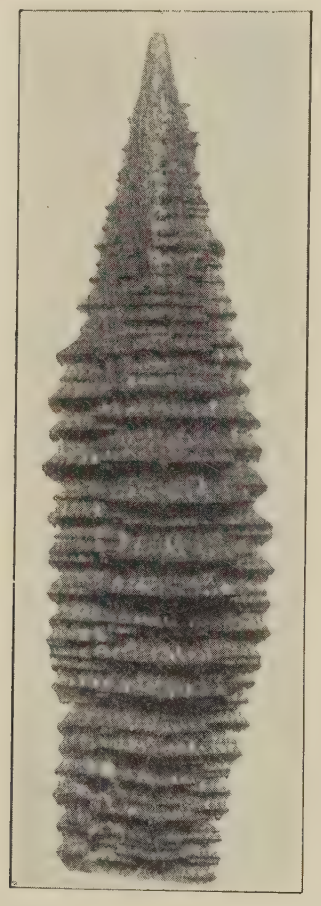
Fig. 106. — Octahedral crystal composed of small cubes. (After H. M. Howe.)

If a considerable mass of liquid iron or of liquid steel could be conceived to exist without its container, suspended in space, and if crystallization started at the center of the solid and proceeded with equal velocity and without hindrance in all directions, the result would be a single very large idiomorphic crystal, a perfect octahedron. Liquid metals, however, must of necessity be held in containers, the form of which they retain after solidification, notwithstanding the crystallizing forces which would cause them to assume octahedral forms. Assuming that the crystallization of liquid steel in its mold could proceed from one center only, and could complete itself without change of orientation, it would be octahedral in its habit and would result in a single very large allotriomorphic crystal, having for its external form the internal form of the mold. Masses of steel made up of but one crystal would inherit the directional properties of single crystals. They would be anisotropic.

Dendrites. — When a metal crystallizes, however, in passing from the liquid to the solid state, crystallization proceeds from many centers or nuclei, and the solidified mass is finally made up of a great many crystals, each one having its own orientation. In the case of iron and steel, if the crystallizing forces could have free play, a perfect octahedron would be formed around each nucleus and the solidified metal would consist of many juxtaposed octahedra. Opposing and disturbing factors intervene, however, such as surface tension, and contact with neighboring crystals likewise in process of formation, which prevent the crystals from assuming regular geometrical forms. In other words, allotriomorphic and not idiomorphic crystals are produced. The mechanism of their formation remains, however, octahedral in character. The

disturbing factors mentioned above cause each individual octahedral growth to increase more rapidly in some directions than in others and, generally, elongated crystallites known as "dendrites" are obtained as in Figure 107. They are also called, because of their appearance, "pine" or "fir-tree" crystals. Such fully developed dendrites are generally found in the "pipes" of large ingots hanging to the roof, like stalactites (Fig. 108). Belaiew describes dendrites as elongated aggregates of octahedra.

Solidified masses of iron or steel, therefore, are made up of a great many dendrites closely interlocked (Figs. 109 and 110). While each crystal possesses directional



(Fig. 107. — Steel dendrites. (Reduced one half.)

Fig. 108. — Steel dendrites in sinking head of large ingot. (After Tschernoff.)

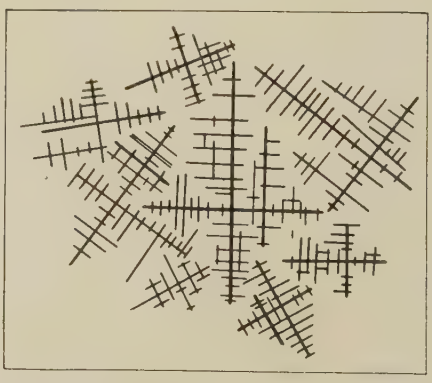


Fig. 109. — Dendritic segregation in steel. (After Tschernoff.)

properties, while it is anisotropic, the mass as a whole may be considered isotropic, i.e. possessing uniform properties in all directions. Directional properties may indeed be imparted to steel as later explained, but this is not due to the anisotropy of the small crystals of which it is made up. It should be borne in mind that the number, size, and form of these crystals, and therefore the properties of the castings, will necessarily be influenced by a number of factors, such as composition, initial casting temperature, rate of solidification, etc. It should be further observed that the cool-

ing action of the walls of the mold has a tendency to impart a "radial" or "columnar" structure to the casting (Figs. 111 and 112), the main axes of the external dendrites being normal to the walls.

It should not be expected that the physical properties of such a casting will be uniform throughout. Test pieces cut from the portions of the casting having a radial dendritic structure will of necessity exhibit different properties from those possessed by test pieces cut from the central portion where the dendritic growth has not been so powerfully influenced by the cooling action of the walls. Steel castings are necessarily structurally heterogeneous.

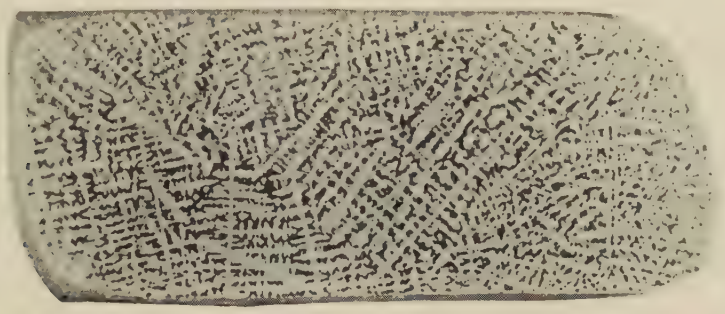


Fig. 110. — Dendritic segregation in steel. Magnified 2 diameters. (By V. N. Krivobok, in the author's laboratory.)

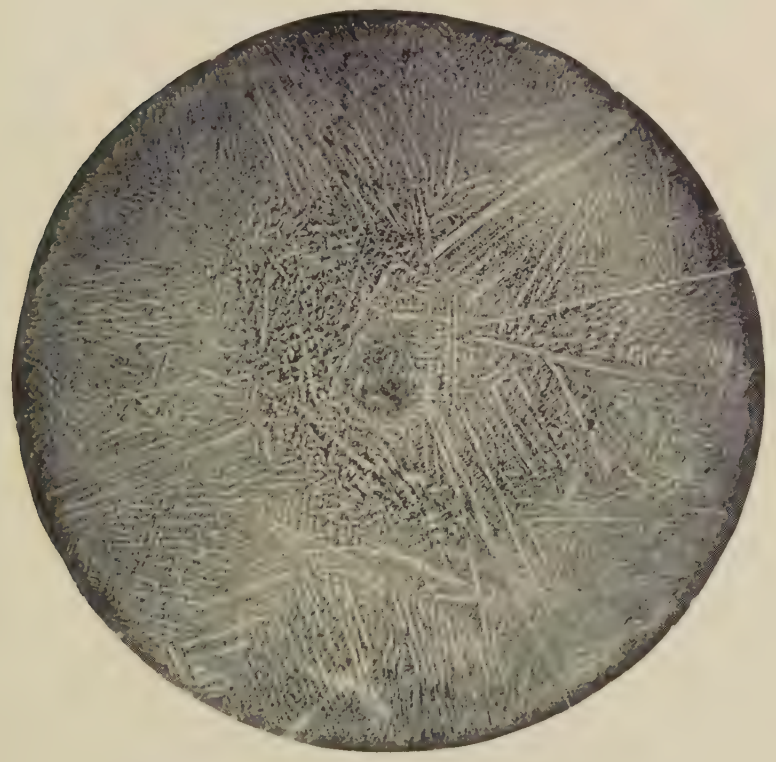


Fig. 111. — Radial dendritic crystallization in steel.

When it will be shown that the dendritic segregation which accompanies the formation of dendrites cannot be effaced by subsequent heat treatments, and that its influence persists even after mechanical working, the importance of its study will be readily appreciated.

Mechanism of Dendritic Growth. — Let us assume a single dendritic crystal in process of formation (Fig. 113). It is believed on very good ground that the primary

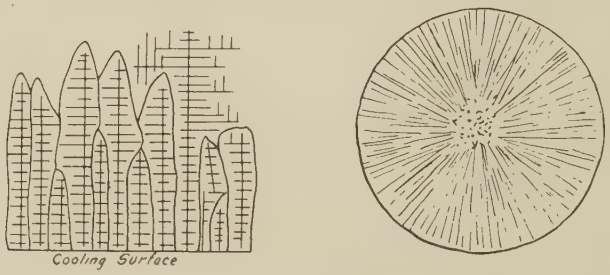


Fig. 112. — Sketch showing the formation of radial or columnar structure in steel castings. (After Tschernoff.)

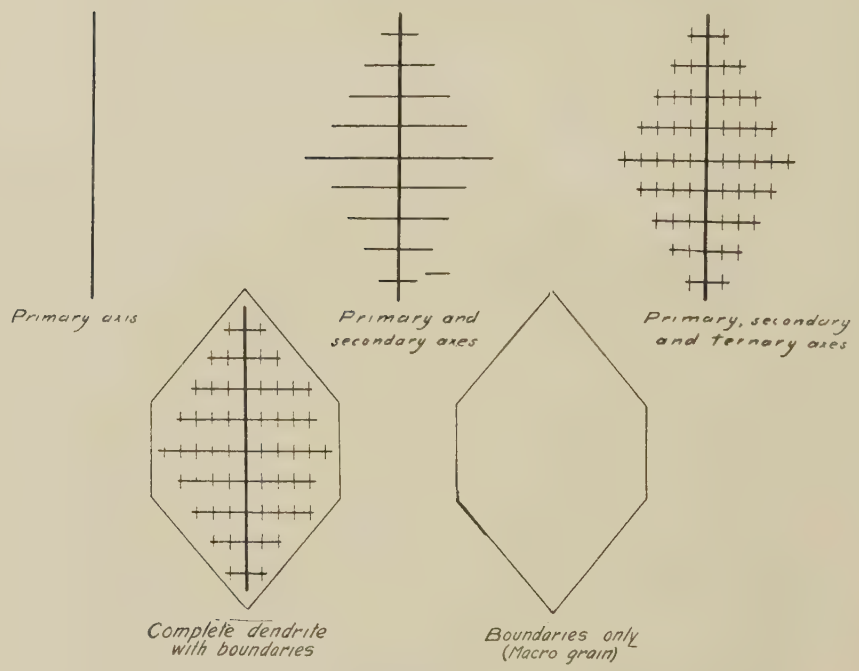


Fig. 113. — Diagrammatic sketch showing the growth of a dendrite.

axis forms first and that this is followed quickly by the appearance of secondary and ternary axes. These axes grow and thicken through gradual deposition of cubic or octahedral particles of solid metal until, finally, the interstices between them are filled up in a like manner and the dendrite is completed. Its external shape will necessarily be influenced by eventual contact with neighboring dendritic growths and boundary lines should exist between them (Chapter I, Fig. 11). It is, however, only

occasionally that these boundary lines can be brought out as in Figure 114. If the iron is chemically pure, the dendrite will necessarily be *chemically homogeneous* in all its parts, and will form at a *constant temperature*, namely, at the solidification point of iron. If we accept Rosenhain's theory in regard to the existence of an amorphous film or cement between crystals formed from the liquid state, then we must assume that each dendrite is enclosed within an amorphous membrane or bag.

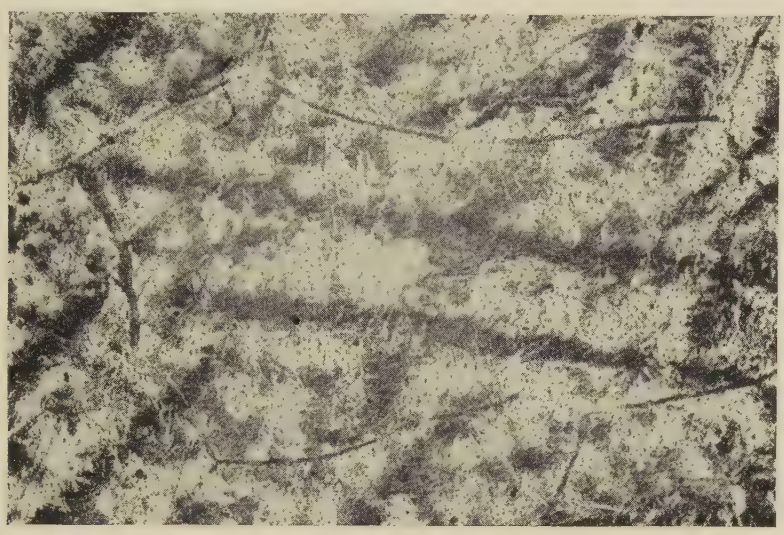


Fig. 114 — Dendrites and boundaries. × 74. (By V. N. Krivobok, in the author's laboratory.)

Detection of Dendritic Growth. — Whenever it is possible for crystals to grow freely, without hindrance from neighboring growths, as for instance in pipes of large ingots (Fig. 108), the dendritic character of the crystallization of iron and steel is clearly revealed. A mass of steel, however, is composed of closely interlocked dendrites and to study its crystallization we must examine polished and suitably treated plane surfaces. Such sections should have the appearance shown in Figure 110. When the dendritic character of the crystallization of steel is clearly revealed, these dendrites and their boundaries are generally so large that they can be observed with the naked eye. The structure is then said to be *macroscopic*, to distinguish it from structures so small as to require the use of a microscope for their detection, that is from *microscopic* structure. We talk, therefore, of macrostructure and of microstructure. The dendritic structure of iron and steel may properly be called "primary structure" and the large grains enclosed within the dendritic boundaries "primary grains." They are generally macroscopic in size, hence we may also talk of macro- and of micro-grains.

The possibility of bringing out the dendritic structure of steel through some suitable treatment of polished sections should be considered. It would seem as if there should be no difficulty in revealing the existence of boundaries between adjoining dendrites because, even in chemically pure metals, those boundaries, if they do not consist of amorphous cement, mark at least changes of crystalline orientation. As already mentioned, however, these boundaries are often very difficult to bring out.

An etching treatment to be effective must necessarily be selective in its action, and in order that it may be selective, the sample under study must be chemically or physically heterogeneous. In the absence of such heterogeneity, selective action by the reagent is impossible and the structure remains hidden. Assuming a dendrite, therefore, perfectly homogeneous in all its parts, physically and chemically, its structure could not be brought out by etching methods. It should be the case with chemically pure iron. When so-called chemically pure iron is considered, however, it is well to remember that such purity is hardly obtainable and that a very small proportion of impurity, possibly little more than a trace, may suffice to produce in the dendrite the necessary heterogeneity required for the selective action of the reagent. It should be further considered, as previously mentioned, that while iron may be reported free, or practically free, from the ordinary impurities, it may still contain some gases held in solution, and this may suffice to produce dendritic heterogeneity.

Dendrites of Solid Solution. — Let us assume a metal or metalloid M′ dissolved in a metal M, and let us assume the soluble component M′ to have a lower melting point than the solvent M. As soon as the solidification range of the alloy is reached, dendrites begin to form at many centers, or nuclei, throughout the cooling mass. Let us consider a single dendrite and follow the mechanism of its formation (Fig. 113). The main axis of the crystal will be the first one to appear and it will be considerably richer in the high melting point constituent, that is in the metal M, than the liquid from which it forms. Secondary and ternary axes will follow in turn *as the temperature of the alloy continues to fall* and these will contain more of the more fusible metal than the main axis but still less of it than the molten metal. Finally, the interstices between the axes will solidify and will contain more of the low melting point metal M′ than the axes. In other words, the formation of a dendrite of a solid solution implies a gradual segregation of the low melting point constituent as the dendrite grows, the portion of last solidification being the richest in that constituent. The boundaries between adjoining crystalline growths, since they are the last to solidify, should contain more of the fusible constituent than any portion of the dendrites themselves. If the boundaries between the dendrites are occupied, as some believe, by amorphous metal or cement, it seems obvious that this amorphous material must be much richer in the low melting point metal than the original alloy. We lack evidence, however, that this is actually the case. The mechanism of the formation of solid solutions, therefore, necessarily implies the production of chemically heterogeneous dendrites. The segregation producing this heterogeneity may be called *dendritic segregation.*

While this heterogeneous dendrite is in the process of formation, however, the phenomenon of diffusion asserts itself and tends to produce chemical homogeneity through the migration of some metal M from the parts in which it abounds to portions deficient in that constituent, and in a like manner migration of some of the metal M′ from the fillings to the axes. This diffusion continues probably on cooling below solidification and is promoted by a slow solidification, long sojourn at high temperatures, and slow cooling. Complete diffusion would efface altogether the dendritic segregation and a chemically homogeneous dendrite would be obtained. It would then be impossible, as previously explained, to disclose by etching methods the dendritic crystallization, since selective action could not take place. Impossibility of bringing out a dendritic structure in an iron or steel casting must be considered as an indication of a chemically pure metal or of a solid solution freed by

diffusion from dendritic segregation. Dendritic segregation always occurs when a solid solution forms and complete diffusion is very rare. While diffusion may decrease to a considerable extent dendritic segregation it does not efface it completely and the dendrites at room temperature remain chemically heterogeneous.

If the dendrites of a solid solution are chemically heterogeneous, that is if their axes have a different chemical composition from the fillings, it becomes possible to bring out the dendritic structure through the selective action of suitable etching reagents. In the case of iron-carbon alloys, for instance, some copper etching reagents may cause a deposition of copper on the axes while the fillings remain unaffected (Fig. 110).

Dendritic Segregation in Iron-Carbon Alloys. — The fact that the dendritic structure of steel castings can generally be readily revealed by suitable etching treat-

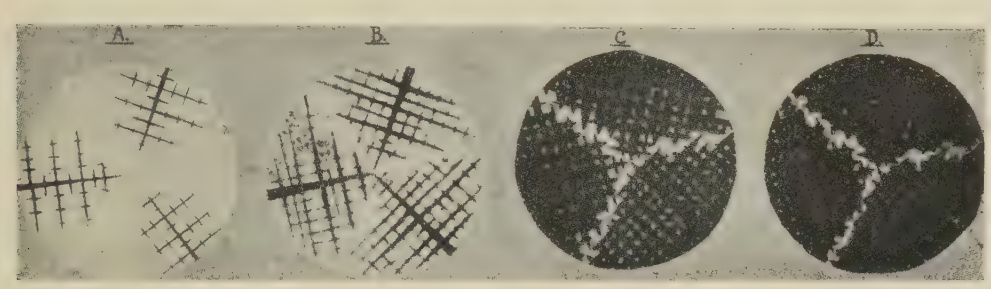


Fig. 115. — Diagram representing the gradual growth of three separate dendrites. (Stead.)

ments is an indication that the dendrites of steel are chemically heterogeneous, that is that the dendritic segregation has not been completely eliminated by subsequent diffusion. It is important to know what constituents are chiefly responsible for this dendritic segregation. We may confine our attention to the three constituents which form with iron solid solutions, namely, carbon, phosphorus, and silicon. Stead claimed long ago that phosphorus was chiefly, if not altogether, responsible for dendritic segregation. This view was generally accepted and is still the prevailing one today.

Stead depicts this primary crystallization in Figure 115, which represents the gradual growth of three separate dendrites. The dark crystallites in A feed and develop out of liquid, abstracting the iron and concentrating the carbon in portions that still remain liquid. The white junctions in C and D represent the last portions of liquid metal, rich in carbon, also sulphur and phosphorus, if any happens to be present. Stead writes: "The fine fir-tree crystallites, containing probably a fraction of the amount of the carbon in the liquid steel, grow steadily forward from the cold surfaces of the containing molds. The crystallites develop branches in three directions corresponding to the axes of the cube, and these branches throw out similar branches themselves. Eventually parts of the most fusible portions are trapped between the branches and are the last to solidify. When there is much phosphorus or some sulphur in the metal, they are always present together with an excess of the carbon in the last residue of metal that remains liquid, and although in cooling down, after the liquid has solidified, the excess carbon diffuses out of it into the purer part, the sulphides and phosphides do not, but remain fixed, and can generally be detected in the solid metal."

According to Stead the main axes contain comparatively little phosphorus, the secondary and ternary axes a larger amount, and the fillings a still greater quantity. While diffusion may cause a decrease of phosphorus segregation, it cannot erase it completely and the dendrites at room temperature remain heterogeneous as to phos-

Fig. 116

Fig. 117

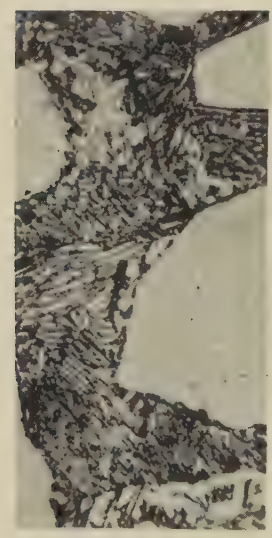


Fig. 118

Fig. 119

Dendritic segregation in steel containing 0.39 per cent carbon and 0.17 per cent phosphorus. (V. N Krivobok, in the author's laboratory.)

Fig. 116. — Etched with nitric acid. Magnified 4 diameters.
Fig. 117. — Same as Fig. 116. Magnified 65 diameters.
Fig. 118. — Same as Fig. 116. Magnified 1000 diameters.
Fig. 119. — Same steel etched with Le Chatelier's reagent. Magnified 85 diameters.

phorus distribution. On etching polished sections with some copper reagents, copper is deposited on the axes which are comparatively free from phosphorus, while it fails to be deposited on the fillings which contain considerably more phosphorus. Dendritic structure is in this way revealed. Stead claims further that phosphorus expels carbon from the portions of the dendrites where the former predominates into portions containing little phosphorus, that is it expels carbon from the fillings and concentrates it in the axes.

The following experiment affords a striking confirmation of the claims that phosphorus produces persistent dendritic segregation and that carbon migrates from the portions rich in phosphorus, namely the fillings, to segregate in the axes, which contains relatively little phosphorus. Using armco iron, a steel ingot was prepared containing 0.17 per cent carbon and 0.39 per cent phosphorus. It was found that on etching this steel with the usual solution of nitric acid and alcohol, a very clear dendritic structure was revealed (Fig. 116). Upon closer investigations, it was discovered that the axes were made of pearlite, while the fillings, undoubtedly rich in phosphorus, were free from carbon (Figs. 117 and 118); hence the possibility of bringing out a dendritic structure by nitric acid etching. After treatment with the Le Chatelier reagent, a similar dendritic structure is obtained (Fig. 119) through the copper having deposited on the phosphorus-free ferrite lamellæ of the pearlitic axes, while the impure ferrite constituting the fillings was not affected, except for the ferrite immediately surrounding the pearlitic axes where it is freer from phosphorus, thus producing an intense coring effect.

The conclusions seem warranted that, on solidifying, the phosphorus, by locating in the fillings of the dendrites, produced intense and persistent dendritic segregation, and that on cooling, the phosphorus caused the carbon to leave the fillings and to collect in the axes, resulting in pearlitic axes and ferrite fillings. While we have here a strong indication that phosphorus produces persistent dendritic segregation and that it is capable of expelling carbon from the regions where the former abounds, it would not be wise to infer that phosphorus alone is responsible for persistent dendritic segregation, because such segregation has been found repeatedly in steel practically free from phosphorus.

The author's experiments, however, have failed to confirm Le Chatelier's contention that oxygen rather than phosphorus is the cause of persistent dendritic segregation.

Disregarding for the moment what element or elements are responsible for persistent dendritic segregation and therefore for the possibility of revealing by etching the dendritic character of the crystallization of steel, it may be considered as firmly established that after solidification all steels are composed of closely interlocked dendrites (Fig. 110). If we refer to Fig. 120, in which the steel portion of the iron-carbon diagram, fully described in Chapter XXV, has been reproduced,[1] it will be noted that the dendrites formed as the alloy cools from its liquidus AB to its solidus ACD. In the complete absence of carbon these dendrites necessarily form at a constant temperature, namely, at the melting point of pure iron. As the carbon increases, the distance between liquidus and solidus, that is the solidification range, increases and becomes maximum at about 1.00 per cent carbon. From 1.00 to 1.70 per cent carbon it remains practically of the same length. The question may reasonably be asked

[1] The possible formation of delta iron on solidification in steel containing less than some 0.35 per cent carbon is not indicated in the diagram.

whether the length of the solidification range has any influence on the size of the dendrites — whether a long range of solidification promotes the formation of more or of fewer dendrites; whether the number of dendrites in eutectoid steel, for instance, with its wide range of solidification is greater or less than the number of dendrites in hypo-eutectoid steel. While there is good ground for believing that the dendrites of eutectoid steel and of hyper-eutectoid steel are smaller than those of hypo-eutectoid

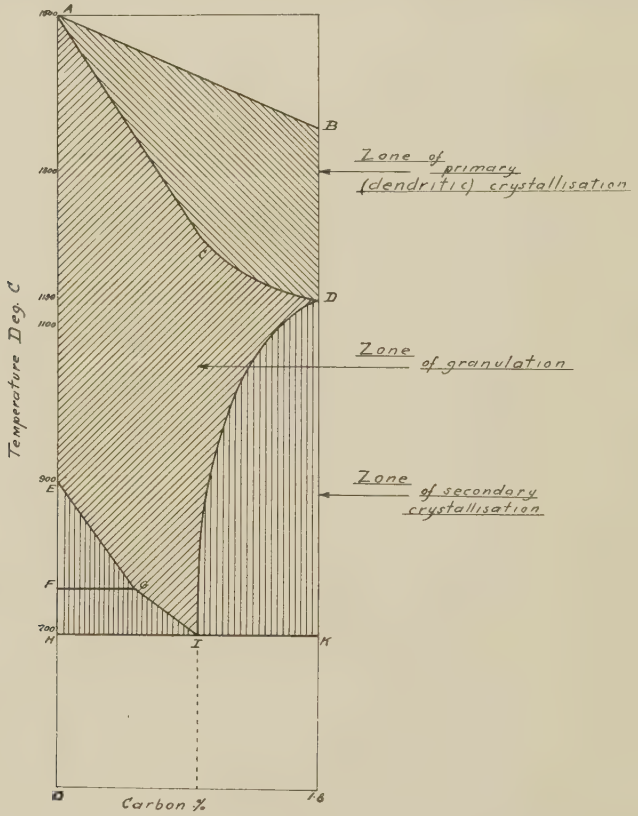


Fig. 120. — Steel portion of the iron-carbon equilibrium diagram.

steel, doubt still exists as to whether this difference is due to differences in the solidification ranges of the steels or to differences in their carbon content.

Granulation of Dendrites. — If the dendritic structure of steel resulting from solidification underwent no modification or transformation on further cooling, all steels at room temperature would consist of interlocked austenitic dendrites, that is dendrites of a solid solution of carbon in gamma iron. Although their properties would undoubtedly vary somewhat with their carbon content and the size and form of the dendrites, they would possess the characteristics of the solid solution austenite. They would be very resistant to abrasion, very difficult to machine, and they would be non-magnetic. They would resemble Hadfield's manganese steel and would have a limited range of application.

On cooling from the solidus to room temperature, however, very important transformations occur which impart entirely new properties to the metal. When a sample of carbonless iron or of steel containing a very small amount of carbon is allowed to

cool slowly from the liquid state to room temperature, it is found, as we know, on microscopical examination, after etching with the usual reagents, to be made up of small polyhedral crystals or micrograins. If a little carbon is present, small particles of pearlite will also be formed.

From the foregoing description of the formation of dendrites and of macrograins on solidification it seems evident that these small micrograins must have formed *after* solidification; that they result from a breaking down of the dendrites. This theory, advanced by Belaiew, gives us the only acceptable explanation to date of the relation between the microstructure of steel and its dendritic structure, generally of macro-size. Belaiew argues that when steel cools from the solidus to the thermal critical range the dendrites and the large grains constituted by the boundaries of those dendrites undergo a process of granulation.[1] The granulation zone corresponds to the area *ACDIGE* of the equilibrium diagram (Fig. 120). In cooling through this zone each dendrite breaks up into a number of small (micro) grains, each having its own crystalline orientation. Since they form above the thermal critical range, they are austenitic micrograins. *Such a process necessarily implies the disappearance of the dendrite as a crystalline unit.* In other words, a large allotriomorphic crystal necessarily of constant crystalline orientation throughout has been transformed into a number of small allotriomorphic crystals, every one with its own orientation and, therefore, independent crystalline existence.

An examination of the zone of granulation, that is of the area *ACDIGE* of the equilibrium diagram, reveals the fact that the width of that zone varies greatly in different steels. For carbonless iron it extends from about 1500 to 900 deg. C., covering a range of 600 deg. C. As the carbon increases the granulation zone decreases slightly. For eutectoid steel, it still covers a range of 500 deg. C. (from 1200 to 700 deg. C.) As the eutectoid point is passed, however, the granulation zone decreases very rapidly. With 1.50 per cent carbon it is reduced to 130 deg. C. (1130 to 1000 deg. C.). With 1.70 per cent carbon the granulation zone disappears. Hypo-eutectoid and eutectoid steels, therefore, have wide granulation zones (500 to 600 deg. C.), while in hyper-eutectoid steel the granulation zone is rapidly narrowed, being finally reduced to zero. It is pertinent to ask whether for like cooling conditions the extent of the granulation zone affects the number of the resulting grains; whether the grains of hypo-eutectoid steel should be for that reason more or less numerous than the grains resulting from the granulation of hyper-eutectoid steel.

The nature of the boundaries surrounding the micrograins resulting from the crystallographic breaking up of the primary dendrites should be considered. Rosenhain in formulating and explaining his amorphous cement theory contends that amorphous iron exists at the boundaries of the micrograins on the ground that they coincide with the last films of metal to solidify. If the granulation theory of Belaiew is correct, Rosenhain must be wrong, since these small grains were not formed during solidification but *below* solidification. Amorphous iron should exist at the boundaries surrounding the dendrites, according to Rosenhain, but not, at least not for like reasons, at the boundaries between the micrograins. It might be argued, however, that amorphous cement exists also at the boundaries between the micrograins on the

[1] One might be tempted to believe that the apparent granulation of dendrites occurs not gradually on cooling below solidification, but quite abruptly when iron-carbon alloys undergo their allotropic transformation on cooling through their critical range, were it not for the fact that it is also observed in metal and alloys which do not undergo allotropic transformations.

ground that when a crystallographic form is transformed into another crystallographic form the substance must first assume the amorphous state and that this state is retained at the boundaries, the final amorphous films surrounding the grains being too thin to assume the crystalline orientation of either of the adjoining grains.

Seeing that the dendrites formed during solidification are entirely destroyed through the granulation they undergo between the solidus and the thermal critical range, it is at first a source of surprise that we should ever be able to bring out a dendritic structure in steel at room temperature. The answer to the apparent enigma is that *the possibility of revealing a dendritic structure through etching treatment does not depend upon the existence of dendrites but upon the existence of dendritic segregation and that while granulation obliterates the dendrites it does not affect dendritic segregation.* The segregating element, whatever it may be, occupies the same portions of the original dendrite even after the latter has undergone granulation. Treatment with the copper reagent, for instance, still results in a deposit of copper on those portions of the polished surface once occupied by dendritic axes since those portions are as free from the segregating element as they were before granulation. The result is a dendritic structure generally of macro-size brought out by suitable reagents and resulting from dendritic segregation and a microstructure resulting from the granulation of the dendrites.

From the close examination of a great many samples treated with the Le Chatelier reagent the author reached the conclusion that *copper is deposited on ferrite only, and that when both ferrite rich in the segregating element and ferrite poor in that element, for brevity of speech impure and pure ferrite, are present, it is on the pure ferrite only that copper is deposited.* In the absence of ferrite, in austenitic and martensitic steels, for instance, it is quite impossible to develop a dendritic structure by means of the Le Chatelier reagent. It does not follow, however, that dendritic segregation does not exist in these steels and that it cannot be revealed by other reagents or other treatments.

Secondary Crystallization and Microstructure. — It has been shown that steel on cooling from the liquid state to its thermal critical range solidifies through the formation of many dendrites, that these dendrites undergo granulation on cooling below the solidus but that the dendritic segregation which necessarily accompanies the formation of solid solutions persists. On reaching the thermal critical range, therefore, all steels are made up of austenitic grains generally of micro-size resulting from the granulation of austenitic dendrites generally of macro-size.

We should now consider what takes place when the steel cools through its thermal critical range to room temperature. The mechanism of that transformation has been described. If the steel is of eutectoid composition, each grain of austenite is converted into a grain of pearlite at the single critical point of that steel. If the steel is hypo-eutectoid a certain amount of ferrite separates from the solid, austenitic solution on entering the critical range until the remaining austenite finally of eutectoid composition is transformed into pearlite at the bottom of the range, that is at the Ar_1 point. If the steel is hyper-eutectoid, it is cementite which separates in a like fashion in cooling through the range.

When carbonless iron cools through its upper critical point, it passes from the gamma to the alpha condition,[1] and since the cube is the crystallographic form of alpha

[1] The author purposely disregards here the possibility of gamma iron transforming into beta iron.

iron while the octahedron is the crystallographic form of gamma iron it must be assumed that each grain undergoes at that temperature a crystallographic transformation. In hypo-eutectoid steel the ferrite which separates on entering the critical range and keeps on separating on cooling through the range, passes immediately from the gamma to the alpha condition and must therefore be made up of small cubic

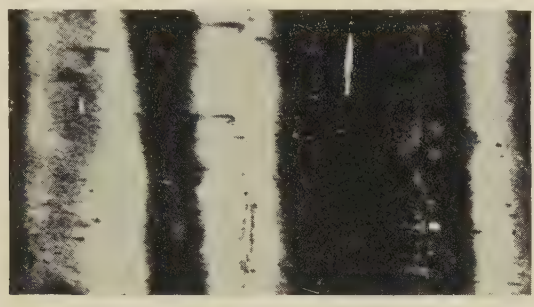


Fig. 121. — Banded structure in rolled steel caused by persistent dendritic phosphorus segregation. × −100.

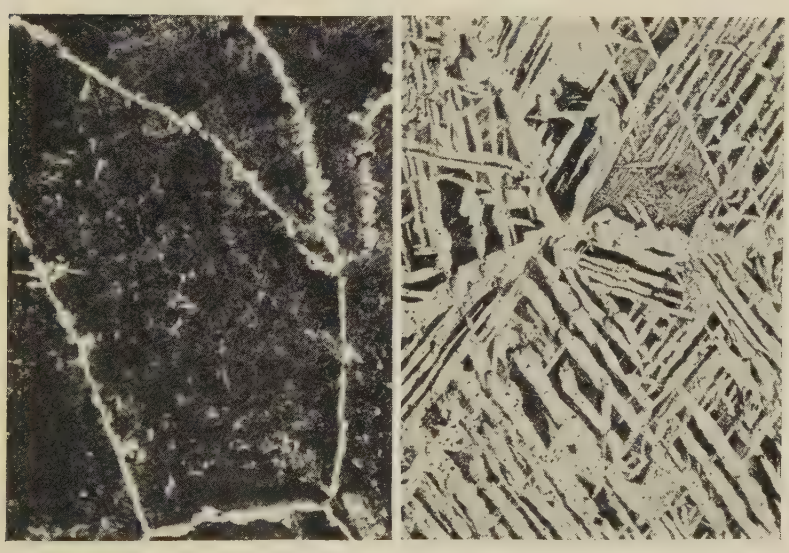


Fig. 122. — Network structure in hypo-eutectoid steel casting. × −65.
Fig. 123. — Widmanstätten structure in hypo-eutectoid steel casting. × −100. (V. N. Krivobok, in author's laboratory.)

crystals. That alpha ferrite is made up of small cubic crystals can be readily revealed by suitable etching tests, as already shown.

Belaiew calls the transformation taking place during the critical range, secondary crystallization.

The speed of cooling through the critical range has a marked effect upon the location and distribution of the separating constituent, ferrite or cementite, and therefore upon the final structure of the casting. Speeds of cooling sufficiently slow to permit

complete separation of the excess ferrite or cementite and final transformation of the remaining austenite into pearlite are alone considered here. Belaiew believes that if the cooling through the range be extremely slow the separating constituent is given the necessary time to reach the boundaries of the crystalline grains and distinct network structures are obtained (Fig. 122). If on the contrary the cooling is too rapid to permit this migration the separating element will be retained to a greater

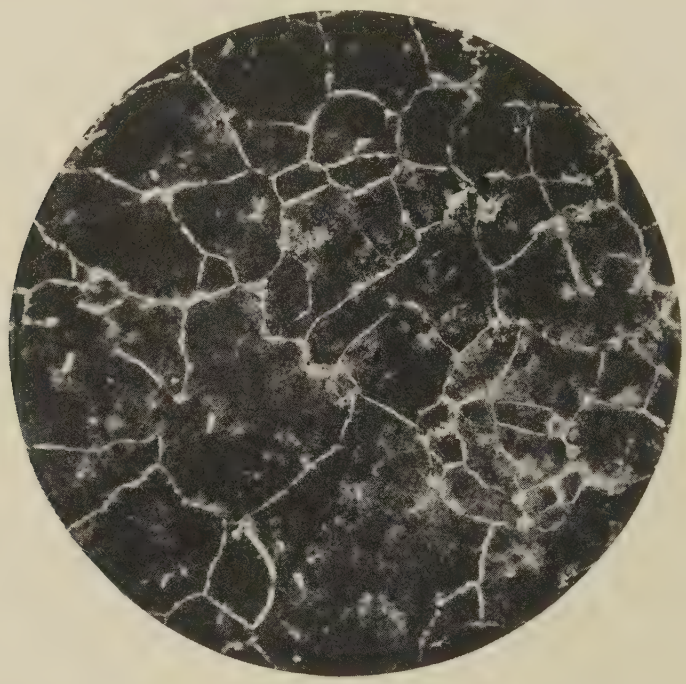


Fig. 124. — Cast steel, 0.50 per cent carbon. Rapidly solidified and cooled. Magnified 28 diameters. (V. N. Krivobok, in the author's laboratory.)

extent in the crystallographic planes of the octahedral crystals and the well known Widmanstätten[1] or cleavage structure will result (Fig. 123).

According to Belaiew a very slow cooling through the granulation zone promotes the formation of the Widmanstätten type of structure on quick cooling through the critical thermal range. To explain the occurrence of the Widmanstätten type of structure frequently found in steel *slowly* cooled through its critical range, Belaiew argues that it is then due to "undercooling"; when the delayed transformation takes place, it does so rapidly, in conformity with the behavior of undercooled systems, hence the separating element is retained in the crystallographic planes.

The author from his own observation holds a different view from that of Colonel Belaiew in regard to the mechanism of the formation of network and of Widmansträtten structures. He believes that when a grain of austenite in cast hypo-eutectoid steel is converted into pearlite in passing through the critical range, ferrite forms *first* at the boundaries (Fig. 124). If the cooling through the range is too rapid

[1] From the name of the French scientist who first observed it in 1808, Alois de Widmanstätten.

to permit further ferrite separation, a network structure will thus be produced, the meshes of which will not be true pearlite, but rather of a sorbitic character, since they still contain ferrite in excess over the eutectoid ratio. That this is the case will, he believes, be confirmed by close microscopical examination. The formation of ferrite boundaries is *followed* by separation of ferrite within the grains along the octahedral crystallographic planes, as previously explained. It can frequently be observed that the first ferrite to separate after the boundaries radiates from them (Fig. 125). Finally and gradually the full amount of ferrite is expelled from the austenite and the entire mesh now consists of pearlite and ferrite, forming a Widmanstätten pattern (Fig. 126). If these views are correct, it follows that in steel castings at least the existence

Fig. 125. — Cast steel, 0.40 per cent carbon. Cooled rapidly through granulation and secondary crystallization zones. Magnified 100 diameters. (V. N. Krivobok, in the author's laboratory.)

of a network structure is indicative of a relatively rapid cooling through the critical range, time having been denied for the complete separation of ferrite, the phenomenon having been arrested in its first stage, namely after the formation of ferrite boundaries. The remaining austenite is then converted into sorbite rather than into pearlite. A Widmanstätten structure, on the contrary, indicates a *complete* separation of the ferrite and results from *slower* cooling through the critical range, the remaining austenite now of eutectoid composition being converted into pearlite. The structure of cast hypereutectoid steel is shown in Figure 127, in which the free cementite has formed partly at the grain boundaries and partly within the grains between cleavage planes. It is not believed that ferrite separating in the center of an austenite grain actually migrates toward the boundaries eventually to be merged with them. It is held, on the contrary, that ferrite within the grains always separates along crystallographic planes and remains *in situ*.

It is hardly necessary to insist on the fact that steel castings exhibiting a network structure cannot be expected to have properties identical to those of castings exhibiting the Widmanstätten structure, although identical in chemical composition.

It is not unreasonable to suppose that the size of the grains formed during granulation and which is probably dependent upon the size of the dendrites may influence the final structure, that is may induce or oppose the network type of structure or the Widmanstätten type. Will a large austenitic grain, for instance, result in a Widmanstätten structure more readily than a smaller grain of the same steel? Seeing that in a large grain the separating constituent would have a longer way to travel to reach the boundary, it seems that this must be the case if we accept Belaiew's theory. Assuming this reasoning to be sound, Widmanstätten structures should form more

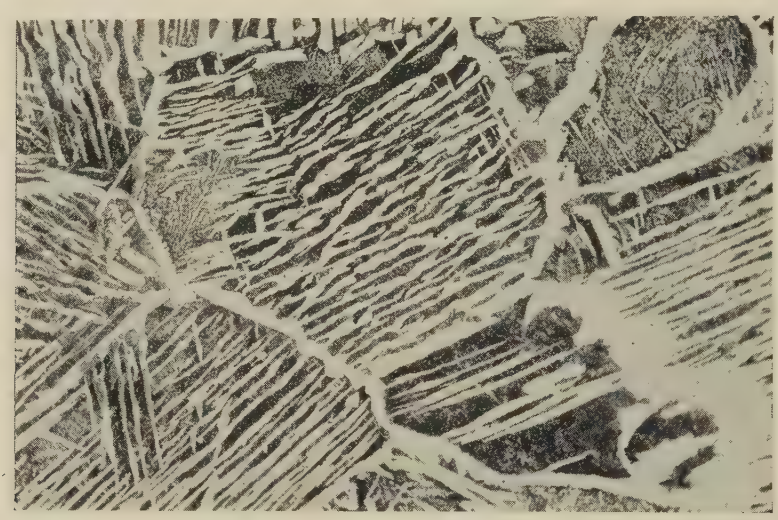


Fig. 126. — Cast steel, 0.50 per cent carbon. Slowly cooled through secondary crystallization zone. Magnified 100 diameters. (V. N. Krivobok, in the author's laboratory.)

readily in hypo-eutectoid than in hyper-eutectoid steels, since the former for like cooling conditions have larger grains.

Many queries of a practical nature come to mind. Will a network structure respond to the annealing treatment more readily than the Widmanstätten structure and should it therefore be promoted in our castings? It is not likely that both behave in a similar manner; one must be preferable and should be induced, and while one type might be more advantageous in castings that are not to be annealed, the other type may be more desirable in castings to be annealed. This opens up an important field of investigation.

Further to clarify and sum up the foregoing discussion let us follow the solidification and cooling to room temperature of carbonless iron, hypo-eutectoid steel, and hyper-eutectoid steel.

Solidification of Carbonless Iron. — Carbonless iron solidifies at 1530 deg. C., when dendrites of gamma iron [1] are formed. The dimensions of the dendrites probably depend on the rate of cooling, a rapid solidification causing the appearance of a greater number of nuclei and therefore of smaller dendrites. If the iron contains some

[1] The author intentionally ignores the possibility advanced by some of the dendrites consisting of delta iron before granulation and of gamma iron after granulation.

impurity subject to persistent dendritic segregation, chemically heterogeneous dendrites will result and their detection will be possible at room temperature through the selective action of a suitable reagent. If it does not contain such impurities, the dendrites will be chemically homogeneous and it will not be possible to reveal by etching the dendritic character of the solidification of the metal. Accepting Rosenhain's theory, the boundaries between adjoining dendritic growths should be occupied by amorphous iron. In cooling from the solidification point to 900 deg. C., every dendrite breaks up into small (micro) grains of gamma iron. The number and, there-

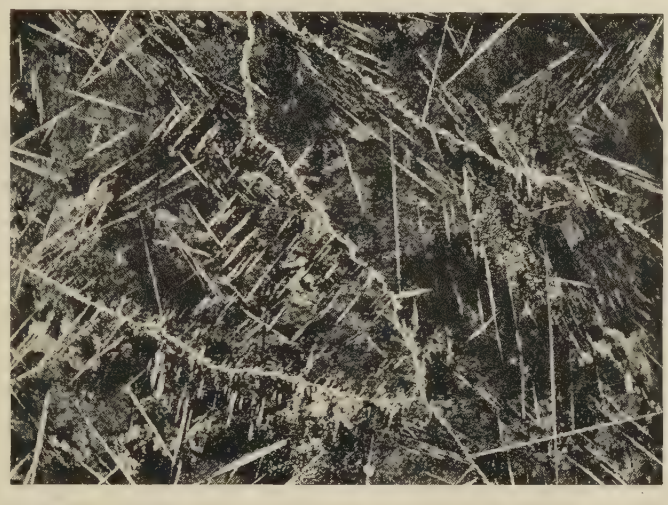


Fig. 127. — Hyper-eutectoid steel. Cast. Free cementite rejected partly to the boundaries and partly between cleavage planes. Magnified 114 diameters. (Boylston.)

fore, dimensions of these grains probably depend upon the rate of cooling through the granulation zone and on the size of the dendrites, which in turn depends upon the rate of solidification. On reaching the upper critical point of pure iron, at about 900 deg. C., each grain of gamma iron is converted into a grain of beta iron, or according to those who deny the existence of beta iron, into a grain of alpha iron, accompanied by a transformation of the octahedral units of gamma iron into the cubic units of alpha iron.

At room temperature, carbonless iron consists of a mass of polyhedral micrograins of alpha iron which have been formed *in situ* at the point Ar_3 through the transformation of as many grains of gamma iron, themselves formed during the granulation zone through the crystallographic breaking up of the dendrites resulting from solidification. If persistent dendritic segregation exists, treatment with the Le Chatelier reagent will result in copper being deposited on the ferrite of the axes because it contains less of the segregated element or elements than the ferrite of the fillings. In this way, although the dendrites themselves no longer exist, the dendritic character of the crystallization of iron stands revealed.

Solidification of Hypo-Eutectoid Steel. — Let us now follow the solidification and cooling to room temperature of hypo-eutectoid steel. Let us assume that it contains 0.50 per cent carbon. The solidification of such steel will begin at about 1475 deg. C.,

and will be complete at 1300 deg. C. (Fig. 120). It will proceed, therefore, as the temperature is falling and will cover a range of some 175 deg. C. Crystallization starts at many centers or nuclei and dendrites are formed, their number and size depending on the speed of solidification, a greater speed probably inducing a greater number of nuclei and, therefore, a greater number of dendrites necessarily of smaller

Fig. 128. — Steel. Carbon 0.55 per cent. Widmanstätten structure. Magnified 6 diameters. (Belaiew.)

size. These dendrites consist of a solid solution of carbon in gamma iron, that is of austenite. In cooling through the granulation zone, which extends from 1300 to 750 deg. C., these austenitic dendrites, generally of macro-size, are converted into small micrograins of austenite, each one with its own orientation, and therefore independent crystalline existence. The number of these grains, and consequently their size, likewise will depend upon the size of the original dendrites and the rate of cooling through the granulation zone. It seems reasonable to assume that a rapid cooling through the zone of granulation will induce the formation of a greater number of grains, necessarily of smaller dimensions. At a temperature of about 750 deg. C., the steel now composed of many austenitic grains of micro-size enters its critical range, which, following Belaiew, we may call the zone of secondary crystallization. At about 690 deg. C., it emerges from that zone transformed into an aggregate of ferrite

and cementite, and presenting a network or a Widmanstätten structure, according to cooling conditions, as previously explained.

If the dendritic segregation which necessarily accompanies the formation of solid solutions has persisted, a treatment with the Le Chatelier reagent will cause a deposition of copper on the free ferrite present in the axes as well as upon the ferrite plates of

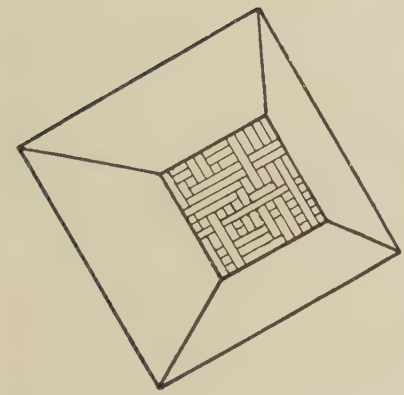


Fig. 129. — Section parallel to the surface of a cube. (Tschermak.)

Fig. 130. — Steel. Carbon 0.55 per cent. Section parallel to the surface of a cube. Magnified 30 diameters. Belaiew.)

the pearlite in these axes, while the free ferrite and the pearlite-ferrite occupying the fillings will not be coated. This is in conformity with the belief previously expressed that copper deposits only on ferrite and that when both pure and impure ferrite are present, it deposits selectively on the pure ferrite and not on the impure ferrite. It follows that although the dendrites no longer exist at room temperature, the presence of dendritic segregation makes it possible to reveal the fact that on solidifying, the steel crystallizes in the form of dendrites.

Solidification of Hyper-Eutectoid Steel. — Let us now consider a hyper-eutectoid steel containing 1.5 per cent carbon. It solidifies on cooling from 1400 to 1150 deg. C. It is then made up of austenitic dendrites, the number and dimensions of which will depend upon the rate of solidification, as previously explained. The granulation zone of this steel extends from 1150 to 1050 deg. C., and in passing through it, each dendrite breaks up into a number of austenitic grains, generally of micro-size, a fast cooling probably inducing the formation of a greater number of grains and consequently decreasing their size. At 1050 deg. C. the steel enters its thermal critical range or range of secondary crystallization. At the point Ar_1, about 690 deg. C., it emerges from that range converted into an aggregate of pearlite and cementite, and presenting one of the two types of cast structures already mentioned. In view of their short granulation zone, hyper-eutectoid steels should be made up of smaller austenitic

grains, for like cooling conditions, on reaching their thermal critical range, than hypo-eutectoid steels, and this is known to be so.

If the dendritic segregation which necessarily accompanied the solidification of the steel has persisted, it will be possible by treatment with the Le Chatelier reagent to reveal the dendritic character of that solidification, although the dendrites themselves

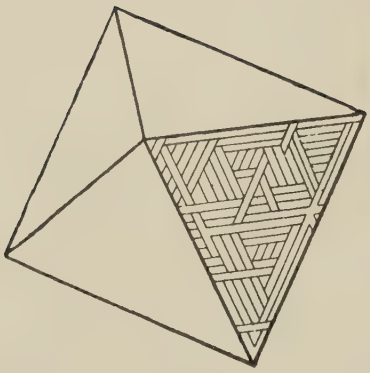


Fig. 131. — Section parallel to the surface of an octahedron. (Tschermak.)

Fig. 132. — Steel. Carbon 0.55 per cent. Section parallel to the surface of an octahedron. Magnified 30 diameters. (Belaiew.)

no longer exist. Copper will be deposited on the ferrite plates of the pearlite present in the axes because of their greater freedom from the segregated element, while it will not be deposited on the ferrite plates of the pearlite in the fillings, owing to their impurity. Copper will not deposit on cementite either in the axes or in the fillings. A dendritic structure is thus revealed.

Belaiew's Investigation. — Belaiew succeeded in a remarkable manner in reproducing the Widmanstätten structure by subjecting carbon steels to suitable treatments. The structures obtained by him in the case of steel containing 0.55 per cent carbon and otherwise of commercial quality are shown in Figures 128 to 135. They are typical structures of steel castings of the same grade but on a much larger scale, for it should be noted that the magnification of Figures 130 to 135 is only 30 diameters, while Figure 128 is magnified but 6 diameters. Figure 128 is a beautiful illustration of that type of structure in which the free ferrite has been rejected both to the grain boundaries forming a sharply outlined network and between crystallographic planes. In Figures 130 to 135 the free ferrite is seen massed between cleavage planes.

Octahedral Crystallization of Austenite. — It will be noted that the ferrite bands shown in Figures 130 to 135 cut each other at right angles or, more frequently, form equilateral triangles. According to crystallographers these are indications that

austenite crystallizes in regular octahedra. That this inference is correct appears to be conclusively proven by the following remarks of Belaiew:

Let us consider an octahedron and let us assume that four systems of lamellæ locate themselves in this octahedron along its crystallographic planes, that is, parallel to the four pairs of its surfaces, a fact that has been long known in the case of meteoric irons.

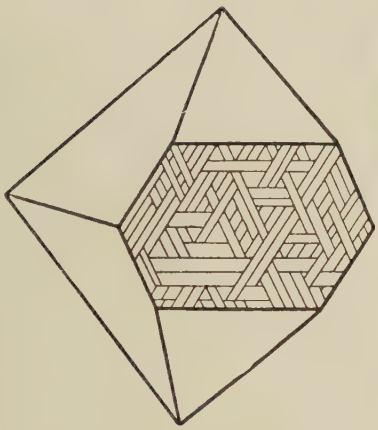


Fig. 133. — Section parallel to the surface of a dodecahedron. Magnified 30 diameters. (Tschermak.)

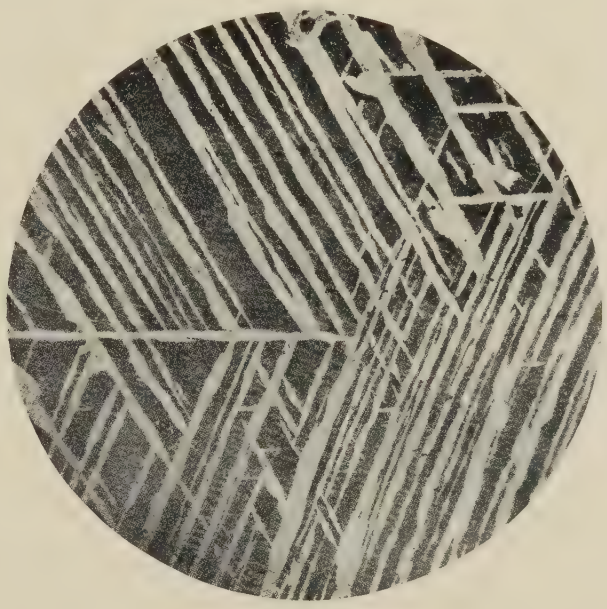


Fig. 134. — Steel. Carbon 0.55 per cent. Section parallel to the surface of a dodecahedron. Magnified 30 diameters. (Belaiew.)

If we now examine any section of the octahedron, we shall find that not only the angles formed by the projections of the lamellæ vary in different sections, but that the number itself of different sections varies likewise from two to four. For instance, when the section is parallel to the surface of the cube, the number of different sections is minimum, that is, two, and in the entire section we find only two systems of lamellæ forming right angles. Figure 129 is a diagram of such section and Figure 130 a corresponding section of the steel.

A section parallel to one of the surfaces of the octahedron will yield equilateral triangles formed by three systems of lamellæ forming 60° angles; the fourth system coincides with the section considered (see Figs. 131 and 132).

In a section parallel to the surface of the dodecahedron, two systems of lamellæ are observed forming an angle of 109° 28′ 16″; the other two systems coincide and divide this angle in half (Figs. 133 and 134). Finally any section will give four different systems cutting each other at different angles (Fig. 135).

All these cases, as we have just seen, can very well be illustrated by different samples of our alloy which, firstly, affords a rather weighty proof of the octahedric crystallization of steel and, secondly, brings out the remarkable analogy of this structure with that of meteorites and warrants us to allude to the synthesis of the structure so called of Widmanstätten . . . this structure is the necessary consequence of the uniform orientation of the elementary octahedra within a volume of greater or less dimension; it is, therefore, in no way related with the carbon content and must be obtained in any alloy of iron and carbon whenever the conditions are favorable to the formation of that structure. . . .

Moreover, in practice this structure is met (although certainly much less developed than in

our alloys) every time that the metal is subjected to an intense heating followed by slow cooling, as is the case with cast steel or, better still, with burnt or overheated steel.

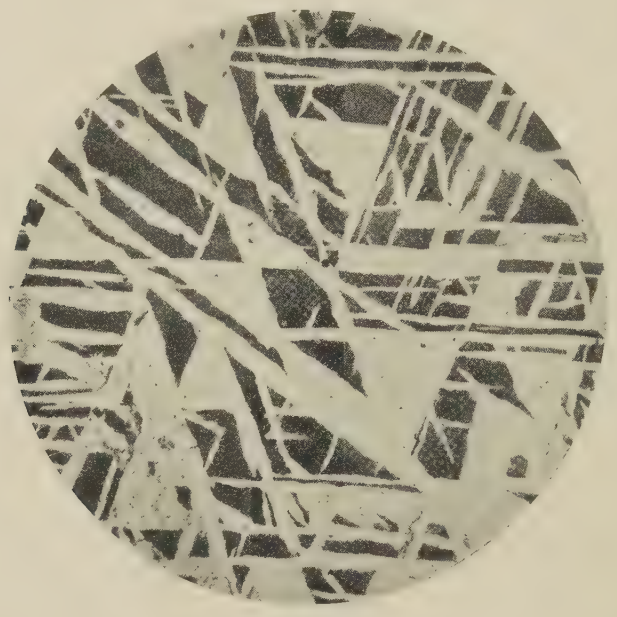
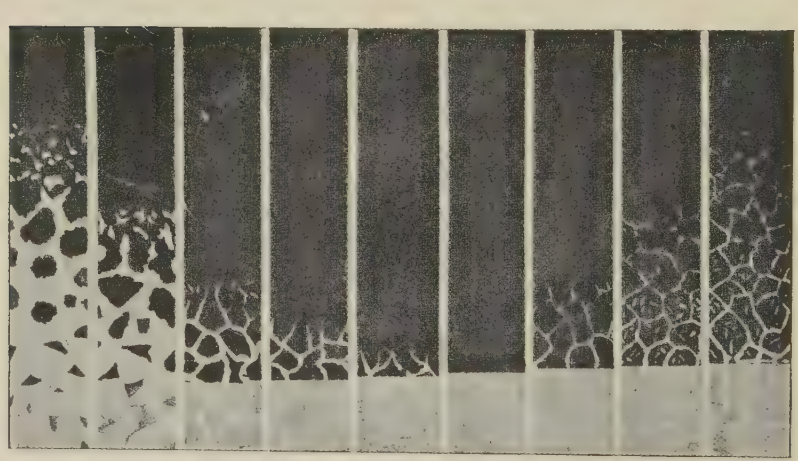


Fig. 135. — Steel. Carbon 0.55 per cent. Four systems of lamellæ. Magnified 30 diameters. (Belaiew.)



A	B	C	D	E	F	G	H	I
			Carbon Per Cent					
0.12	0.20	0.50	0.65	0.75	0.90	1.10	1.40	1.60

Fig. 136. — (Stead.)

The very brittleness of these steels may be due to a certain extent to the uniform orientation of the elementary octahedra which are the cause of that structure.

Let it be noted that in the case of meteorites the length of time during which the metal is maintained at a high temperature is so long that generally but one crystal is formed, that is, all the elementary octahedra formed on solidification have assumed the same orientation. In steel the conditions being less favorable to uniformity of orientation we have several grains.

Fractures of Hypo- and Hyper-Eutectoid Steels. — The rejection of free cementite, like the rejection of free ferrite, makes for coarseness of structure and fracture, from which it follows that cast and slowly cooled hyper-eutectoid steel will be coarser than cast and slowly cooled eutectoid steel, and that the more free cementite it contains, that is the higher the carbon, the coarser it will be. The structure and fracture of hyper-eutectoid steel, however, will generally be decidedly finer than that of hypo-eutectoid steel because of the very small amount of free cementite present in the former compared to the amount of free ferrite in the latter, unless, indeed, the hypo-eutectoid steel be very near the eutectoid composition. This is due to the fact, now well understood, that starting from the eutectoid composition (carbon 0.85 per cent), as the carbon decreases the amount of free ferrite increases rapidly, while as the carbon increases above the eutectoid ratio the amount of free cementite increases slowly and remains small even with high carbon content. Steel with 0.50 per cent carbon, for instance, contains 41.5 per cent of free ferrite, hence its coarseness both of structure and fracture, while steel with say 1.25 per cent carbon contains but 5.8 per cent of coarsening free cementite, hence the relative fineness of both its structure and fracture.

The rejection of the "excess" constituent (ferrite or cementite) and the formation of the final pearlitic structure in steels of varying carbon contents has been interestingly depicted by Stead (Fig. 136). A, B, C, D, and E are hypo-eutectoid steels containing increasing percentages of carbon, F is steel of eutectoid composition, G, H, and I hyper-eutectoid steels of increasing carbon contents. The diagram clearly shows (1) that in hypo-eutectoid steel, as the carbon increases, the rejection of the free ferrite (the white constituent) by the solid solution (the black portion) begins at progressively lower temperatures (the Ar_3 or $Ar_{3.2}$ point) and that the amount rejected decreases steadily, (2) that in hyper-eutectoid steels, with increasing carbon, cementite is rejected in larger proportions and at increasing temperatures (the Ar_{cm} point), (3) that at the Ar_1 or $Ar_{3.2.1}$ point the remaining solid solution (black portion) is converted bodily into pearlite (the shaded portion), (4) that a coarse austenitic structure developed above the Ar_1 point implies the formation of a coarse pearlitic structure below that point, and (5) that with some 0.50 or more per cent carbon the excess constituent frequently forms membranes surrounding pearlite grains and giving rise to so-called network, cellular, or polyhedral structures.

Ingotism. — Howe has suggested the term "ingotism" to designate the structure of cast steel described in the foregoing pages and characterized (1) by large pearlite or sorbite grains and (2) by coarse ferrite or cementite membranes surrounding them and by irregular masses of these constituents located in some of the cleavage planes of the original austenite grains.

CHAPTER XI

THE MECHANICAL TREATMENT OF STEEL

Forged steel objects are manufactured by subjecting the cast metal (1) to pressure exerted by rolls, presses, or dies, or to blows from hammers and (2) by reheating it to various temperatures for various lengths of time and cooling it at various rates. In other words we have to consider (1) the mechanical treatment of steel and (2) its heat or thermal treatment. The machining of steel is not here mentioned since it can evidently have no effect upon the structure and properties of the metal, unless it be a very superficial one.

While the primary purpose of working steel is to shape it into useful appliances and while the primary purpose of reheating it may be, and often is, to impart to the metal such plasticity as will facilitate its being so shaped, both mechanical and heat treatments deeply affect the structure of steel and therefore its physical properties. To this very important subject the next seven chapters will be devoted. We shall first consider the influence of mechanical treatment and then that of heat treatment.

Hot Work vs. Cold Work. — Bearing in mind that steel may be worked as soon as it has solidified as well as at room temperature and at all intermediate temperatures, that is over a range of temperature covering some 1400° C., and that working at a high temperature is generally referred to as "hot working," while working at a low temperature is called "cold working," we naturally desire to know the temperature of demarcation between the two. As later explained, it seems logical to consider as hot working, in the case of iron-carbon alloys, all work performed above the critical range, that is above the A_3, $A_{3\cdot2}$, or $A_{3\cdot2\cdot1}$ points, as the case may be, and to describe as cold working, working performed below that range, that is below A_1. In justification of this procedure it will suffice to point out that working the alloy above its critical range implies working it while it is in the state of solid solution (austenite), and that it recrystallizes as soon as the work ceases, while in working the alloy below its range we are working and deforming an aggregate which does not recrystallize when work ceases, at least as far as the distorted pearlite is concerned. This definition of hot work and cold work is based then chiefly on the ability of the metal to recrystallize when work ceases, which it possesses above the critical range and only in a limited degree, if at all, below that range. The microstructure of cold worked metal remains permanently deformed.

In regard to pure or at least carbonless iron (ferrite), however, it is found, as will soon be explained, that after cold deformation it may recrystallize at a temperature as low as 450 deg. It will also be shown that the more severe the cold deformation the lower the temperature at which it recrystallizes. Following the same arguments, therefore, while placing the demarcation temperature between hot work and cold work for iron-carbon alloys at the critical range, in the case of carbonless iron that

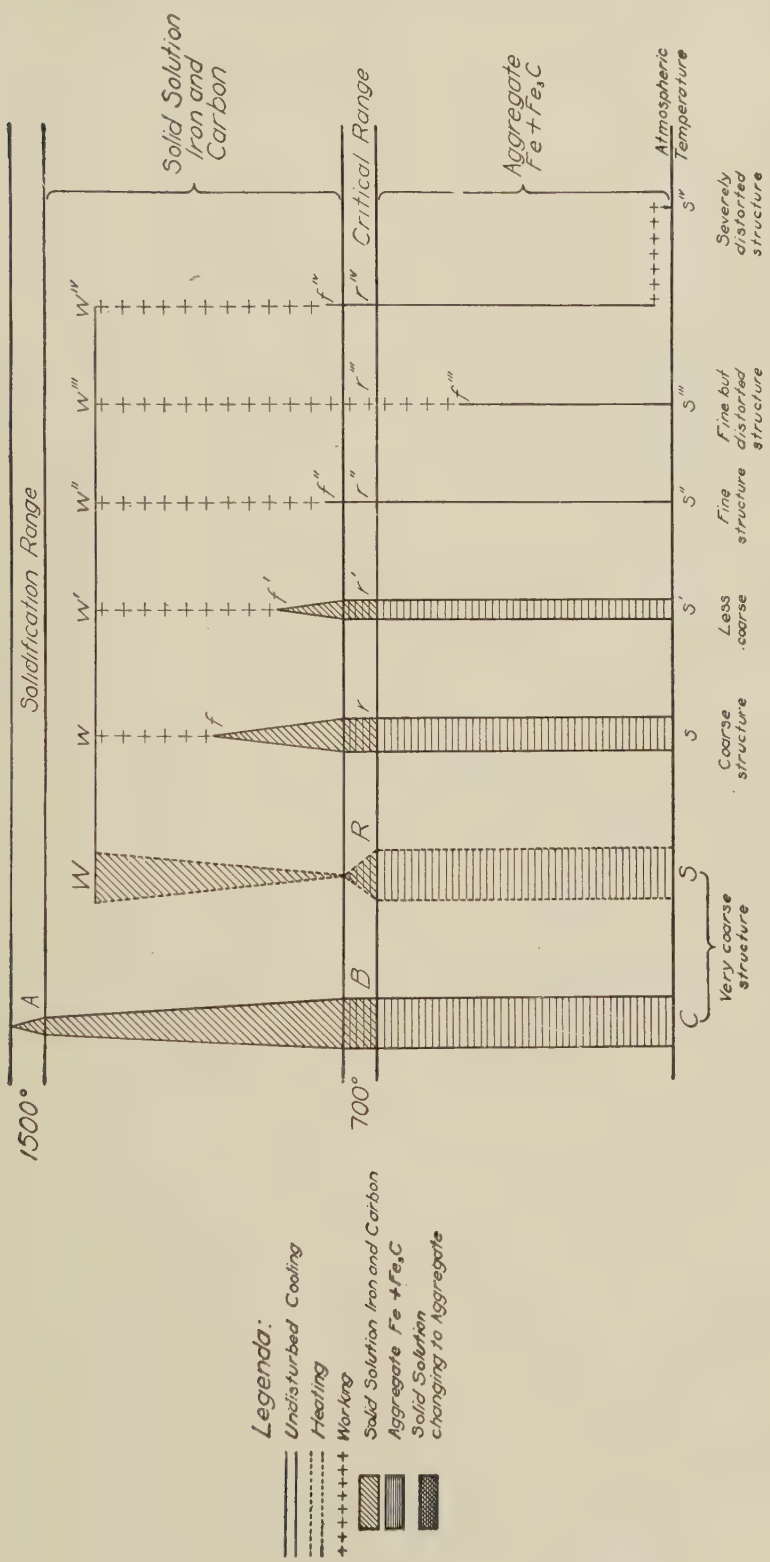


Fig. 137. — Diagram depicting the influence of work upon the structure of steel.

demarcation should be placed between 450 deg. C. and some higher temperature, possibly 700 deg., depending upon the degree of cold deformation.

Hot Working. — Hot working may be applied to steel (1) after it has solidified but before it has cooled to a much lower temperature so that it still possesses the necessary plasticity, or (2) the steel ingot may be allowed to cool to room temperature or at least to a temperature so low that reheating is required as a preliminary step to successful hot working. Let us assume that the steel ingot be allowed to cool to room temperature, that it is then reheated to a temperature well above its critical range and then subjected to hot working.

An attempt has been made in Figure 137 to depict graphically the influence of hot work on the structure of steel. The diagram will be readily understood. The critical range both on heating and cooling is represented by a double line, but the reader will, of course, bear in mind that the critical range on heating does not coincide with the range on cooling and that each range may include one, two, or three critical points, as fully explained in previous chapters. For the present purpose it is preferable to represent both ranges irrespective of the number of critical points included by the two parallel lines shown in the diagram. The solidification range is likewise indicated by a double line. The widths of the shaded areas are intended to be proportional to the grain size resulting from the various treatments; when an area is reduced to a mere line the corresponding grain is very small, i.e. the structure is very fine. As the steel ingot solidifies at A, dendrites are formed and, on further cooling, grains, which are probably the larger the slower the undisturbed cooling to the critical range B. In passing through that range the austenite grains are converted into pearlitic grains with or without rejection of free ferrite or of free cementite according to the carbon content of the steel. On cooling from B to C there is no further growth and the size of the final grain may be represented by the width of the shaded area at C. The metal has now the usual coarse structure of steel castings described in Chapter X. Upon reheating this coarsely crystalline steel ingot from S to R and through its critical range, it is converted from the condition of an aggregate of ferrite and cementite into a nearly amorphous solid solution, so that as the metal emerges from its range it has a very fine structure. As steel just above its critical range, however, would not be plastic enough for hot working and would not afford the necessary range of temperature through which to cool while being worked and still remain, as it should, above the range, it is generally necessary to heat the metal to a much higher temperature, say to some 1200 deg. C. or even more (W in Fig. 137). As the metal is heated from its critical range to this high temperature, it probably crystallizes so that when work begins at w it may have the grain size indicated. This grain growth on heating from R to W is depicted in the diagram. The heavy pressure or blows which are now applied, however, soon break up this crystallization while preventing a new one from forming, so long at least as the work continues sufficiently vigorous, for *undisturbed* cooling is a condition necessary for the ready growth of crystals. As soon as work ceases, however, the metal being now left to cool undisturbedly, if its temperature is then above its critical range, for instance at f, it will immediately begin to crystallize and its crystallization will continue from f to r, that is until its critical range is reached, when it will stop and the austenite grains just formed will be converted into as many pearlite grains with or without rejection of free ferrite or free cementite. The width of the band at s is intended to represent the size of the final grain. It is smaller than the grain of the steel ingot but it is still large.

If work ceases, then, while the metal is still above its critical range, it is evident that it will crystallize and that the resulting grains will be the larger, that is its

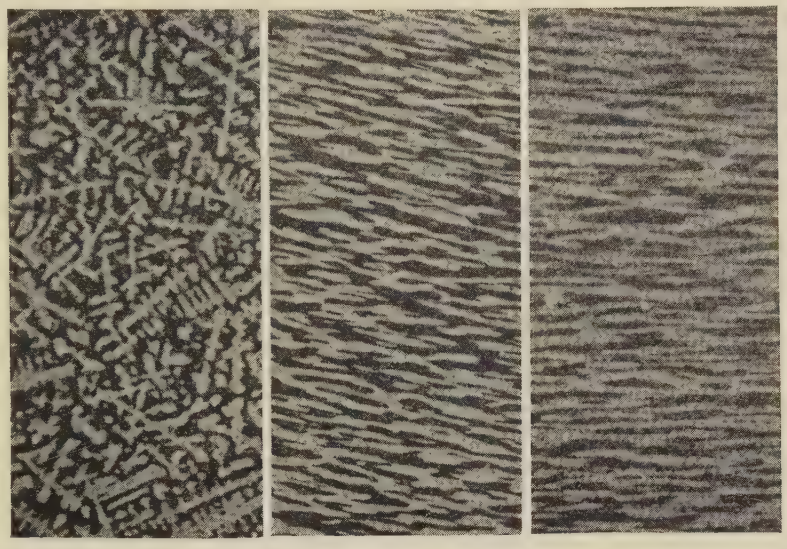


Fig. 138. — Dendritic structure of steel ingot. (Charpy.)
Fig. 139. — Same as Figure 138 after being reduced ⅕ its original cross-section by hot working. (Charpy.)
Fig. 140. — Same as Figure 138 after being reduced to $\frac{1}{30}$ its original cross-section by hot working. (Charpy.)

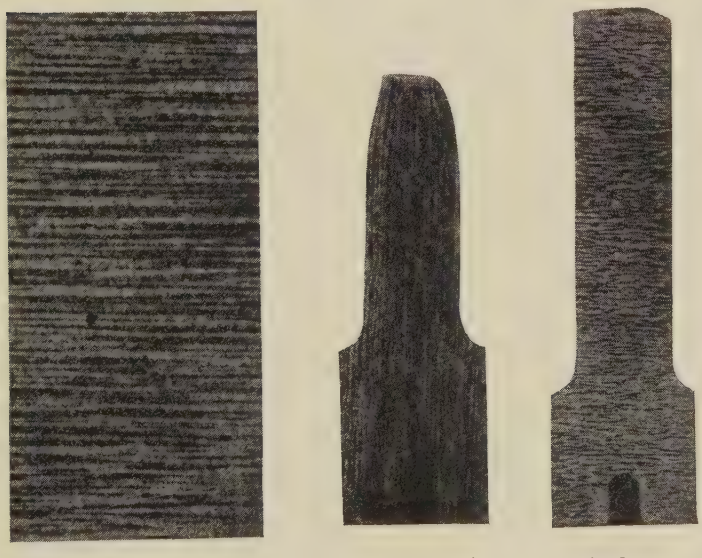


Fig. 141. — Same as Figure 138 reduced $\frac{1}{150}$ its original cross-section by hot working. (Charpy.)
Figs. 142 and 143. — Dendritic segregation in longitudinal and transverse tensile test bars. (Charpy.)

structure will be the coarser the higher the temperature at which the work was discontinued.

Finishing Temperatures. — The temperatures at which work ceases are known as the finishing temperatures, and the above considerations will show the importance

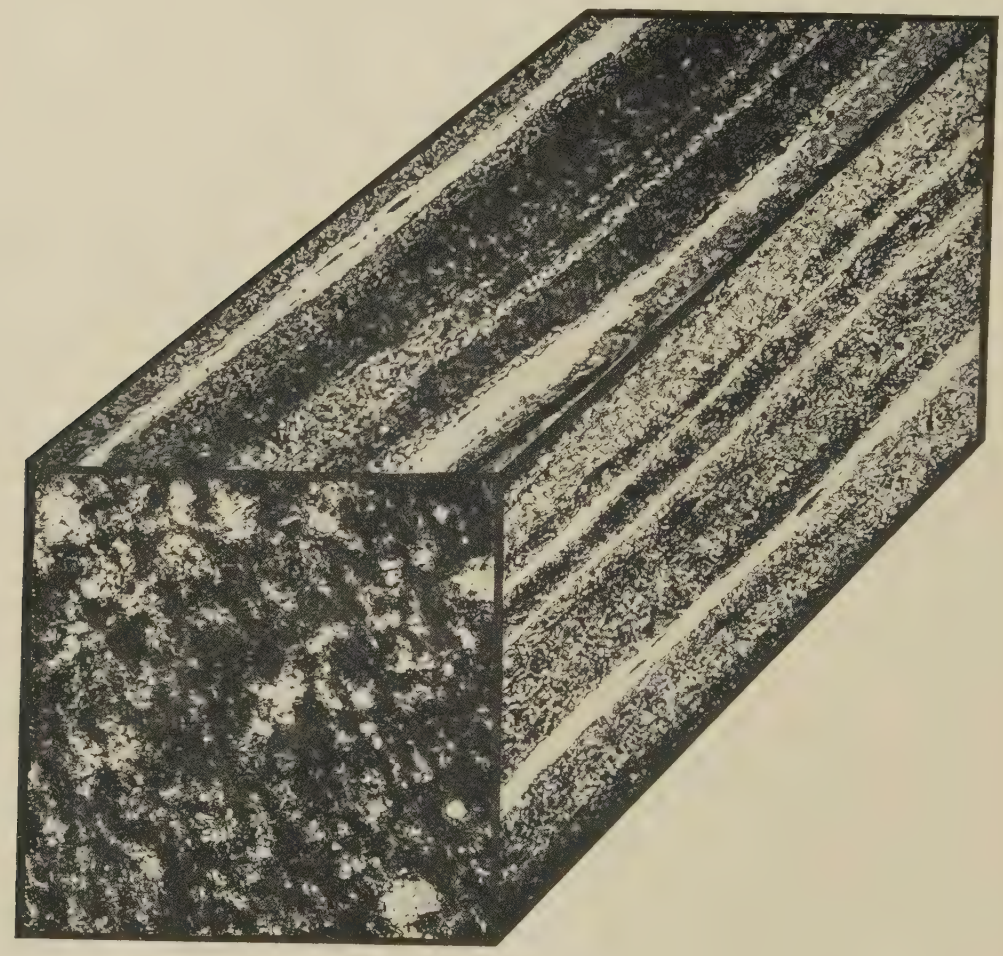


Fig. 144. — Banded structure in forged steel.

of proper finishing temperatures if it be desired to impart to a steel implement the finest grain that it can acquire through working together with the desirable properties inherent to it.

Should hot work be continued, for instance, until the temperature of the metal is but slightly above its critical range, f' in Figure 137, the austenitic grains that will form on undisturbed cooling to the range will be small, so that the final grain of the metal at s' will likewise be small, as indicated by the width of the shaded area. If the finishing temperature is exactly at the critical range, f'', the final grain at s'' will be very fine. If working be continued until the metal has cooled to a temperature lower than its critical range, for instance f''' in the diagram, the structure will be fine since crystallization was prevented while the metal was cooling above its critical

range, but it will be distorted because the effect of working below the range, that is of cold working, is to distort the structure, as explained in the following pages. A distorted structure in turn means decreased ductility and eventually brittleness. It seems evident, therefore, that hot worked steel implements should be finished exactly at their critical ranges or at temperatures but slightly superior or inferior to them.

Dendritic Segregation — Banded Structure — Directional Properties. — It has been explained in the preceding chapter that steel ingots are made up after solidification of closely interlocked heterogeneous dendrites and that while those dendrites probably undergo granulation on further cooling, the dendritic segregation implied by such chemical heterogeneity persists. When steel ingots are subjected to work that is forged or rolled, the portions rich in the segregating elements (the fillings of the dendrites), as well as those poor in these elements (the axes), are elongated in the

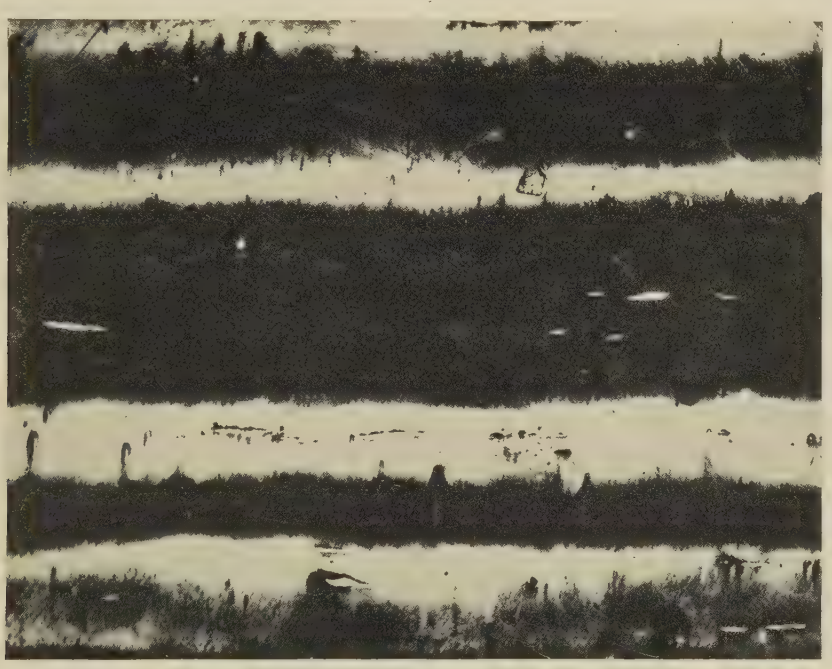


Fig. 145. — Banded structure and "ghosts" in forged steel.

direction of the work, imparting to the hot worked steel the well known laminated appearance readily revealed by macro-etching (Figs. 138–141). The steel seems to be composed of parallel bands. This structural "banding" of steel by hot working is at times very pronounced, as shown in Figure 144, which illustrates the structure in three directions of steel containing 0.50 per cent carbon, and also in Figure 145. It has already been pointed out that when the ferrite bands containing inclusions (the fillings of the dendrites) are very wide they are known as "ghosts" or "ghost lines." Some of these bands contain much of the segregating elements, while others are quite free from them. The Le Chatelier reagent deposits copper on the latter while the former remain little, if at all, affected. Directional properties are in this way imparted to steel by hot working. The tensile strength, elastic limit, and especially the ductility and resistance to shock, will vary much in accordance with the direction of testing, whether it is in a direction parallel to that of the work, at right

angles with it, or in some other direction. In the absence of persistent dendritic segregation such structural orientation should not result from hot working and the metal should not acquire directional properties. Indeed the author is not aware that direc-

Fig. 146. — Hot worked eutectoid steel. Magnified 100 diameters. (Boylston.)

Fig. 147. — Hot worked hypo-eutectoid steel. Carbon 0.50 per cent. Finishing temperature near critical range. Magnified 100 diameters. (E. L. Reed, in the author's laboratory.)

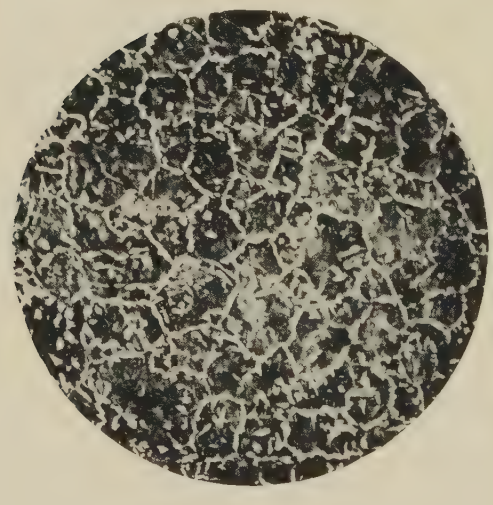


Fig. 148. — Hot worked hypo-eutectoid steel. Carbon 0.50 per cent. Finishing temperature considerably above the critical range. Magnified 56 diameters.

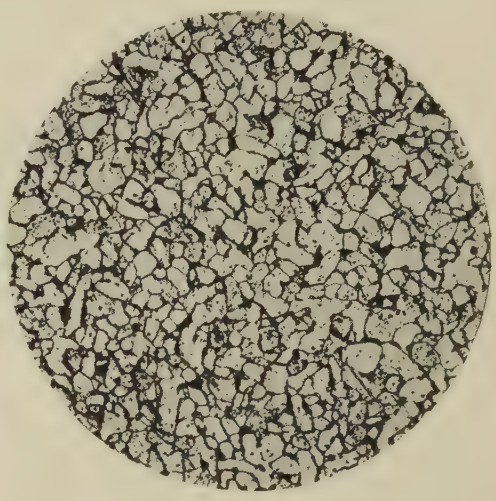


Fig. 149. — Hot worked hypo-eutectoid steel. Carbon 0.10 per cent. Magnified 114 diameters. (Boylston.)

tional properties can be imparted to chemically pure iron by hot work. Obviously, the more pronounced and persistent the dendritic segregation, the more pronounced the directional properties. The directional properties resulting from hot working, combined with dendritic segregation, is further illustrated in Figures 142 and 143.

The test bars were cut respectively in the direction of the work and at right angles. The much greater ductility of the former bar is clearly seen.

It is evident that the physical properties of any rolled or forged article must be deeply affected by this feature of its structure, which in turn is dependent upon the size and heterogeneity of the dendrites formed on solidification. It is a frequent occurrence that two samples of steel of practically identical composition and microstructure exhibit widely different physical properties to the surprise and distress of those concerned. It is believed that if the macrostructures of the samples were likewise examined, the explanation in many cases would be obvious. Steel makers should bear in mind that the structure imparted to the steel ingot during its solidification exerts a lasting effect upon the physical properties of finished articles. They should, the author believes, exert every effort to produce ingots having small dendrites as homogeneous as possible. Purity, of course, especially absence from phosphorus and inclusions, will promote dendritic homogeneity. Rapid solidification should result in smaller dendrites, and slow cooling below solidification should promote diffusion, hence homogeneity. Excessive reduction by hot working should be avoided since it accentuates the directional properties and if carried too far impairs the usefulness of the metal when subjected to transverse stresses both static and dynamic.

Microstructure of Hot Worked Eutectoid Steel. — If eutectoid steel be subjected to hot work until it has nearly reached its critical range (now consisting of the single point $Ar_{3\cdot2\cdot1}$), f'' in Figure 137, it will have a very fine austenitic structure which in cooling slowly and undisturbedly through the critical range at r'' will be converted into a fine pearlitic structure. The metal will then have as fine a structure as can be imparted to it by work alone, followed by slow cooling through the range.

If eutectoid steel be worked until its temperature is still considerably above its critical point (f, Fig. 137), and then allowed to cool undisturbedly, austenite grains begin to form and increase in size as the metal cools to its critical point, i.e. from f to r, when these austenitic grains are converted into as many pearlitic grains. The final grain size therefore will depend upon the temperature at which work ceased and will be the greater the higher that temperature.

The structure of hot worked eutectoid steel is shown in Figure 146 under a magnification of 100 diameters.

Microstructure of Hot Worked Hypo-Eutectoid Steel. — If hypo-eutectoid steel be worked until its temperature is but slightly above its critical range (f'', Fig. 137) and then allowed to cool undisturbedly, small grains of austenite are formed which on passing through the critical range at r'' are converted into pearlite grains with rejection of excess ferrite as now well understood (Fig. 147). When finished at higher temperatures, "network" structures are often produced (Fig. 148), the bulk of the free ferrite forming membranes surrounding grains of pearlite (or of sorbite). Generally speaking the meshes of the network will be the larger the higher the finishing temperature.

In the case of low carbon steel, however, containing say less than 0.30 per cent carbon, the proportion of free ferrite is so large, i.e. the ferrite net so thick, that the structure consists of particles of pearlite embedded in a matrix of ferrite (see Fig. 149, and also Fig. 136, A and B).

It remains to be considered whether working hypo-eutectoid steel between the A_3 (or $A_{3\cdot2}$) point and the A_1 point should be regarded as hot or cold working. When such steel cools through this range while being forged, ferrite is thrown out of solu-

tion and immediately deformed in the direction of the work as well as the austenite. When the work ceases in this range, however, both the deformed ferrite and deformed austenite recrystallize. It seems consistent, therefore, to consider all work performed above the A_1 point as hot work.

Microstructure of Hot Worked Hyper-Eutectoid Steel. — If hyper-eutectoid steel be hot worked until its temperature is very near its critical range (*f''*, Fig. 137) and then allowed to cool undisturbedly, small austenite grains are formed which on cooling through the range are converted into small pearlite grains with rejection of free cementite, as shown in Figure 150. If the work be stopped at a temperature considerably above the critical range (*f*, Fig. 137), the final pearlite grains will be

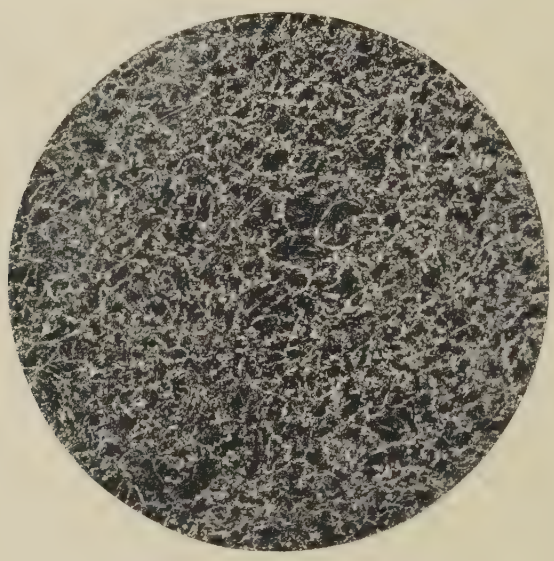


Fig. 150. — Hot worked hyper-eutectoid steel. Carbon 1.50 per cent. Finishing temperature near critical range. Magnified 100 diameters. (G. A. Reinhardt, in the author's laboratory.)

larger while the free cementite will be located chiefly at the grain boundaries, a network structure being produced. It will be evident that a close relation exists between the size of the meshes of these network structures and the corresponding finishing temperatures.

Sorbite. — High magnification of the structure of the meshes of both hypo- and hyper-eutectoid steel described in the foregoing pages often fails to reveal the characteristic features of pearlite, namely, (1) sharply defined parallel plates alternately of ferrite and cementite and (2) a constant or nearly constant carbon content. The structure of these meshes instead remains indistinct and presents a granular rather than a lamellar aspect (Fig. 151). It is also frequently noted in connection with these network structures that the full amount of free ferrite or of free cementite has not been rejected, the pearlitic grains having retained some of the constituent in excess of the eutectoid ratio. To this imperfectly developed pearlite the name of sorbite has been given (Osmond) and quite universally adopted. It will be apparent that the formation of sorbite results from a relatively quick cooling through the critical range,

time being denied for the crystallization of distinct lamellæ of ferrite and cementite and, in the cases of hypo- and hyper-eutectoid steel, for the rejection of the full amount of free ferrite or free cementite. The cooling in air of hot worked pieces, especially when of small size, is often sufficiently rapid to cause the formation of sorbite rather than of pearlite.

The production and nature of sorbite will be dealt with at greater length in another chapter. It should be mentioned here, however, that while sorbite is less ductile

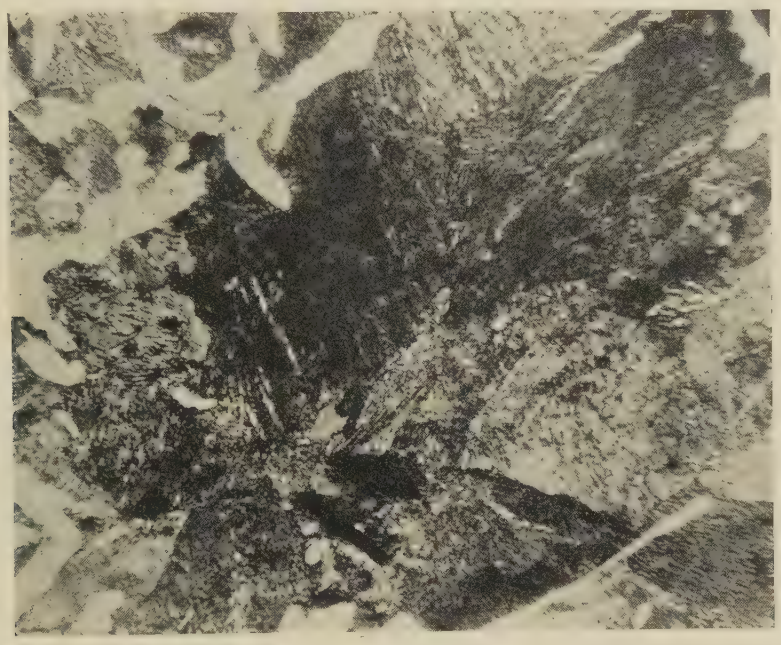


Fig. 151. — Hot worked steel. Carbon 0.50 per cent. Magnified 650 diameters.

than pearlite it has a higher tenacity, higher elastic limit, and greater hardness (hence greater wearing power). When these qualities are required, in hot-forged objects, they may consequently be obtained, although necessarily at the sacrifice of some ductility and softness, by hastening the cooling through the critical range, after work has ceased, when sorbitic rather than pearlitic steel will be produced.

Hot Working of Steel vs. Its Critical Range. — In conducting the hot working of steel so as to impart to the metal the finest grain that can result from finishing at suitable temperatures, it is generally necessary only to consider its lower critical point on cooling, namely, Ar_1 or $Ar_{3\cdot2\cdot1}$. The following considerations will justify this statement. In the case of hypo-eutectoid steel if the working be continued while the metal cools from its upper point or points to its lower point, it will make for fineness of structure by preventing a coarse massing of the free ferrite, while the latter if deformed at all will recrystallize on undisturbed cooling. The same reasoning applies, with greater force, to the hot working of hyper-eutectoid steel from its upper point (denoting the formation of free cementite) to its lower point $Ar_{3\cdot2\cdot1}$. Greater fineness of structure will result with very little, if any, distortion of the free cementite.

It is apparent, therefore, that in order to secure the finest grain obtainable through mechanical refining without appreciable structural distortion steel objects should be finished slightly above their lower critical point, that is in the vicinity of 700 deg. C. for all grades of commercial carbon steel.

Critical Plasticity at the A_3 and $A_{3\cdot2}$ Points. — Dr. D. C. Lee and the author have shown that when iron and hypo-eutectoid steel undergo their allotropic transformation at the A_3 or $A_{3\cdot2}$ points, they become abnormally plastic. This has been explained in Chapter IX.

Cold Working. — By the cold working of steel is meant in these pages, working it while its temperature is below its critical range. It will now be shown that the

Fig. 152. — Cold worked hypo-eutectoid steel. Carbon 0.30 per cent. Magnified 150 diameters. (Buck, Correspondence Course student).

effect of cold working upon the properties of the metal is very different from that of hot working. This should not be a cause for surprise if it be borne in mind that steel above its critical range is in a condition totally different from its condition below it. Above the critical range we have to deal with a solid solution of iron and carbon, below it with an aggregate of pearlite and ferrite (or cementite). The solid solution existing above the range will crystallize if allowed to cool undisturbedly and it has been shown in the foregoing pages that working in this range, i.e. hot working, is effective in preventing or at least retarding this crystallization, thus imparting a smaller grain to the metal. The aggregate existing below the range, on the contrary, exhibits no tendency to crystallize during slow and undisturbed cooling, because this aggregate was formed and fully developed while passing through the range, the size of its elements, that is its coarseness, depending (1) upon the coarseness of the solid solution immediately before its transformation and (2) upon the time occupied in cooling through the range. Working this aggregate, therefore, as it cools to room temperature, or working it while at room temperature, i.e. cold working it, results

in *distorting* the existing structure, chiefly through the stretching or elongation of its crystalline elements (free ferrite, free cementite, pearlite) in the direction of the forging, and such distortion in turn means decreased ductility and eventually extreme brittleness. It has already been explained that the ferrite present in the aggregate distorted by work below the critical range may recrystallize provided the cold work

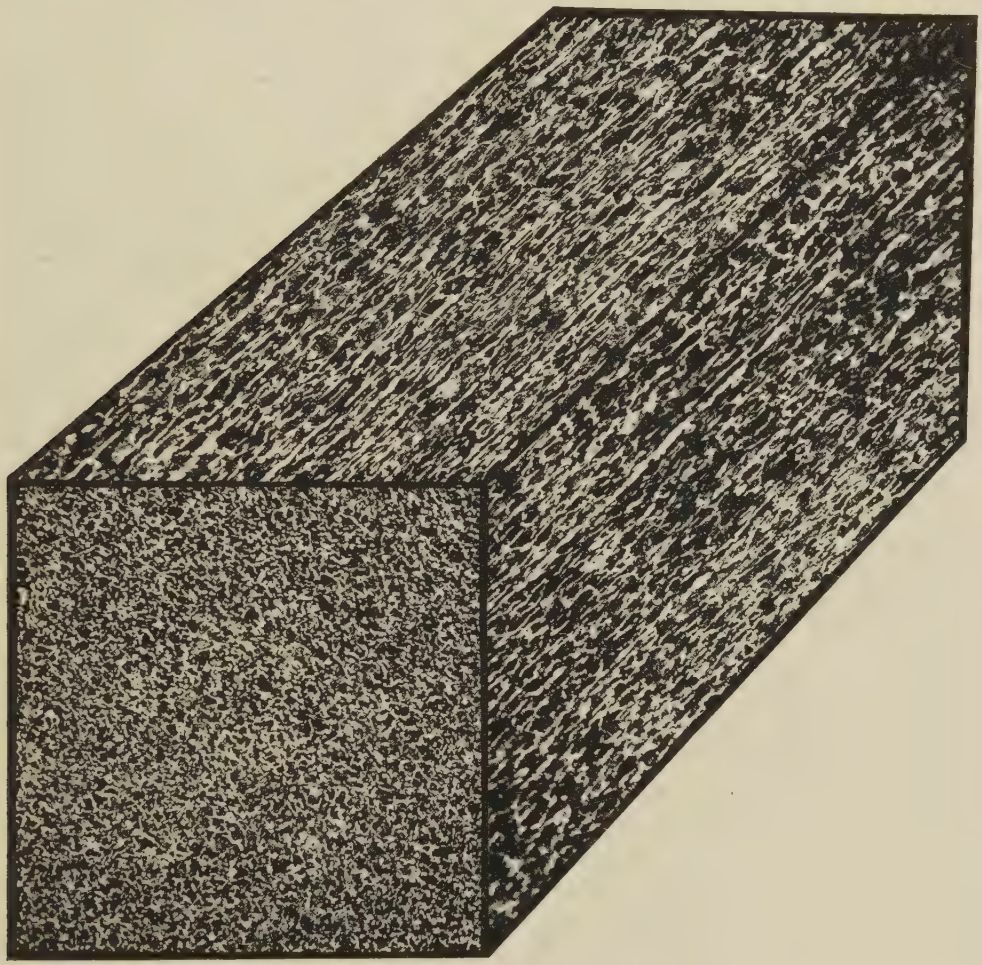


Fig. 153. — Hypo-eutectoid steel, cold worked.

ceases above its recrystallization temperature, the lowest limit of which is at about 450 deg. C. The distorted pearlite particles, however, remain distorted. The effect of cold working upon the structure of steel is illustrated in Figure 152 and in "three dimensions" in Figure 153, in the case of hypo-eutectoid steel. It is also depicted in the diagram of Figure 137. While the structural distortion caused by cold working is very slight near the critical range of the metal, it rapidly increases as the temperature decreases, becoming very pronounced at room temperature. The manufacture of wire by cold drawing affords a familiar instance of the effect of work performed at atmospheric temperature both on the structure and properties of the metal. It is well known that after the wire has been passed through several dies it becomes so

brittle that annealing is necessary in order to make further reduction in size possible, the annealing operation removing the structural distortion and brittleness produced by working at atmospheric temperature.

Cold Worked Steel Castings. — Dr. Krivobok subjected to cold working a small steel *casting* containing 0.50 per cent carbon. The distortion of the components of the

Fig. 154. — Steel casting, cold worked. Carbon 0.50 per cent. Magnified 350 diameters (V. N. Krivobok.)

aggregate, i.e. of free ferrite and of pearlite, is clearly shown in a "three dimensions" diagram in Figure 154. The distortion of the pearlite areas is illustrated under a higher magnification in Figure 155. The structure of the original casting is shown in Figure 156.

Cold Working vs. Physical Properties. — The cold working of iron and steel affects deeply many of the properties of these metals, its action increasing in intensity as the temperature falls, being therefore more severe at room temperature. The elastic limit, tensile strength, and hardness are increased in a marked degree, while the ductility as represented both by elongation and reduction of area is reduced,

extreme brittleness being eventually produced. Cold working decreases the density of iron and steel while the annealing of the cold worked metals increases their density.

Fig. 155. — Steel casting, cold worked. Carbon 0.50 per cent. Magnified 500 diameters. (V. N. Krivobok.)

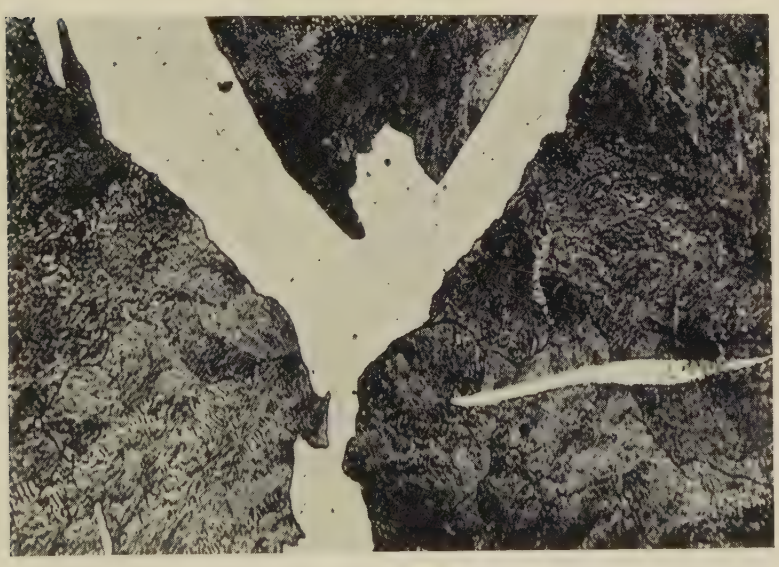


Fig. 156. — Steel casting. Carbon 0.50 per cent. Magnified 350 diameters. (V. N. Krivobok.)

Both magnetic permeability and remanence are diminished by cold working while the coercive force is increased. Electrical resistance is slightly increased as well as the solubility in acids and the tendency to rust or to corrode. The specific heat does not appear to be affected.

It has been explained in Chapter III that the straining of metals does not involve an actual distortion, an elongation for instance of their crystalline elements, but rather a yielding through successive crystalline slips. It should also be recalled that many believe in the existence of amorphous iron produced by severe straining, as in cold working, and that the influence of that operation on some of the properties of the metal, as mentioned above, may be accounted for in accordance with that hypothesis.

Mechanical Refining. — It would seem as if with the use of pyrometers at least it should be a relatively simple matter to finish steel objects very near the desirable temperature and thus secure for them the best structure that can be imparted by work alone. Upon reflection, however, it will be manifest that the problem is on the contrary an insoluble one, for the reason that unless the objects are of very small cross-sections, it is quite impossible to finish them so that their temperature will be uniform throughout, the central portions being necessarily hotter than the outside. Should the forging be so conducted that the temperature of the outside is very near the critical range, the center, being materially hotter, will coarsen on cooling, while if the implements, on the contrary, are finished so that their center may have the fine structure produced by ceasing the work at the proper temperature, their outside must necessarily suffer from cold working. The limitations of work alone as a means of imparting the best possible structure to steel are therefore quite evident.

While a uniformly fine grain cannot be imparted to steel objects of considerable size through hot working alone, the value of hot work as a means of refining the structure of steel remains very great as exemplified by the structure of properly hot-forged steel when compared with the structure of steel castings of similar composition. The finer grain imparted to steel by working has been called by some writers "mechanical" refining to distinguish it from the refining produced by heat, i.e. from "thermal" refining. In practice hot work should be so conducted, that is the finishing temperatures so regulated, that the central portions of the finished implements will not suffer unduly from the coarsening influence of too high a finishing temperature, while at the same time the outside will not suffer unduly from the effect of cold working. The natural tendency of rolling and other forging mills is to finish work at too high temperatures for the simple reason that the metal is then more plastic and consequently requires less power for its working. In some manufactures, however, and especially in the rolling of rails, the importance of proper finishing temperatures has been given careful attention and the rolling operation so modified as to deliver rails of much finer grain, and therefore better physical quality, than formerly.

Besides its important grain-refining influence hot work further improves the quality of steel by closing and, if the carbon be low enough, welding, the blowholes and otherwise increasing its soundness and by removing cooling strains.

Summary. — The action of hot and of cold working upon the structure and the physical properties of steel may be summed up as follows:

The hot working of steel ingots, that is work performed above the A_1 point, (1) closes blowholes and promotes soundness; (2) increases at first the density by closing the blowholes, and then decreases it; (3) destroys the preëxisting coarse crystallization and produces a grain which will be the smaller, other things being equal, the nearer the finishing temperature to the critical range, this being known as mechanical refinement; (4) causes a deformation of the dendritic segregation which results in a banded structure and directional properties; (5) first increases tensile strength and

ductility both longitudinally and transversely, but on further reduction, while it may continue to increase the elongation and reduction longitudinally, it now decreases those properties transversely very decidedly. It also increases resistance to shock longitudinally while decreasing it transversely. These results are the more marked the more impure the steel, that is the more intense the dendritic segregation existing in the ingots.

Cold work, that is working below the A_1 point, (1) causes a permanent deformation of the components of the aggregate (ferrite, cementite, and pearlite), resulting in increased hardness, strength, and elastic limit and in decreased ductility; (2) decreases density, magnetic permeability, and remanence, increases the coercive force, increases slightly the electrical resistance, diminishes resistance to corrosion and to the action of acids.

CHAPTER XII

HEAT TREATMENT

GENERAL CONSIDERATIONS

Object of Heat Treatment. — In submitting iron and steel implements to heat treatment, it is sought to impart to those metals through the action of heat certain desired physical properties. These results are obtained because of the structural changes induced by heat. In studying the effect of heat treatment, therefore, we should carefully consider (1) the structural condition of the object before treatment, (2) the structural changes occurring during treatment, and (3) the structural conditions permanently retained. We should further bear in mind that the physical properties of steel implements do not depend solely upon their chemical composition and their microstructure but upon their macrostructure as well. In our study of the structural changes brought about by heat treatment, therefore, the macrostructure or dendritic segregation should receive as much attention as the microstructure. Steel objects having substantially the same composition and the same microstructure are frequently reported as varying much in physical properties. This causes surprise if not dismay. As mentioned in the preceding chapter, if the macrostructure resulting from dendritic segregation was examined with the same care as the microstructure, many of these apparent enigmas might be explained.

It has been seen that iron-carbon alloys, and therefore all grades of steel, consist above the critical range of a solid solution of carbon or of the carbide of iron, Fe_3C, in gamma iron called austenite, and that on sufficiently slow cooling through the range these solid solutions are converted into aggregates of pearlite and ferrite in hypo-eutectoid steels and of pearlite and cementite in hyper-eutectoid steels. The steels are then in their pearlitic condition, which is the stable one at room temperature, and they possess the maximum softness and ductility and minimum strength consistent with their composition. If steel when cooling from its austenitic condition to room temperature necessarily assumed a pearlitic structure, that is if its transformation was necessarily complete, its heat treatment would be of relatively little importance and it would not be possible to produce those remarkable and widely different sets of properties which distinguish so sharply iron-carbon alloys from other metals and alloys and place them at the head of industrial metals in a class by themselves.

By regulating the speed of cooling through the thermal critical range, it is possible to retain in various degrees the steel but partially transformed through the formation and retention of so-called transition constituents called martensite, troostite, and sorbite, or through the formation or retention of aggregates of two of these constituents, as, for instance, pearlite and sorbite, sorbite and troostite, troostite and martensite. Each of these constituents has its own physical properties which it imparts to the steel.

Passing from martensite, which is the hardest, strongest, and least ductile constituent, and which is generally considered to mark the first step in the austenite-pearlite transformation, requiring therefore very rapid cooling through the range for

its retention, to pearlite, which is the softest, most ductile, and weakest, troostite and sorbite in the order named are less hard, less tenacious and more ductile than martensite, corresponding to more advanced stages of the transformation.

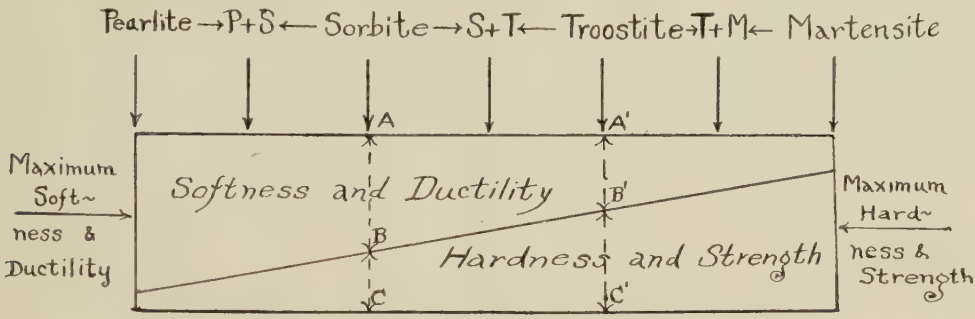


Fig. 157. — The constituents of steel and their physical properties.

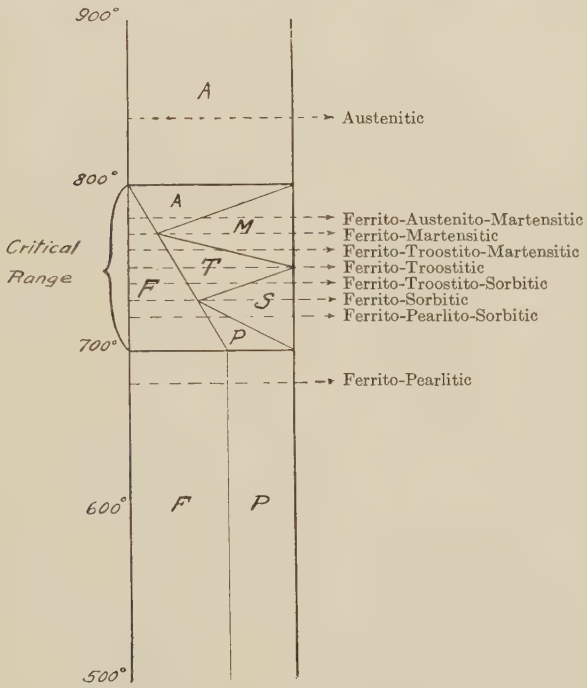


Fig. 158. — Diagram depicting the mechanism of the structural transformation in steel containing 0.30 per cent carbon on slow cooling through the critical range.

These facts are summed up graphically in the sketch of Figure 157, in which the softness and ductility of sorbite, for instance, is represented by the distance AB, and its strength and hardness by BC, the softness and ductility of troostite by A′B′, considerably smaller than AB, and its strength and hardness by B′C′, considerably greater than BC, and so on for the properties of pearlite and martensite as well as those of mixtures of neighboring constituents.

Rate of Cooling vs. the Structure of Steel. — An attempt has been made in Figures 158 and 159 to illustrate graphically the mechanism of the very great influence ex-

erted upon its structure and physical properties by the speed with which steel cools through its thermal critical range. Steel containing some 0.30 per cent carbon has been selected but the same reasoning would apply to any other hypo-eutectoid steel as well as to hyper-eutectoid steel. In the latter case, however, free cementite instead of ferrite would form, if time be given, in cooling through the range.

It is shown in Figure 158 that while the steel above its critical range is composed entirely of austenite and while, after very slow cooling, it contains nothing but ferrite and pearlite, in passing through the range the transformation of the solid solution austenite into the ferrite-pearlite aggregate is not sudden but gradual, several

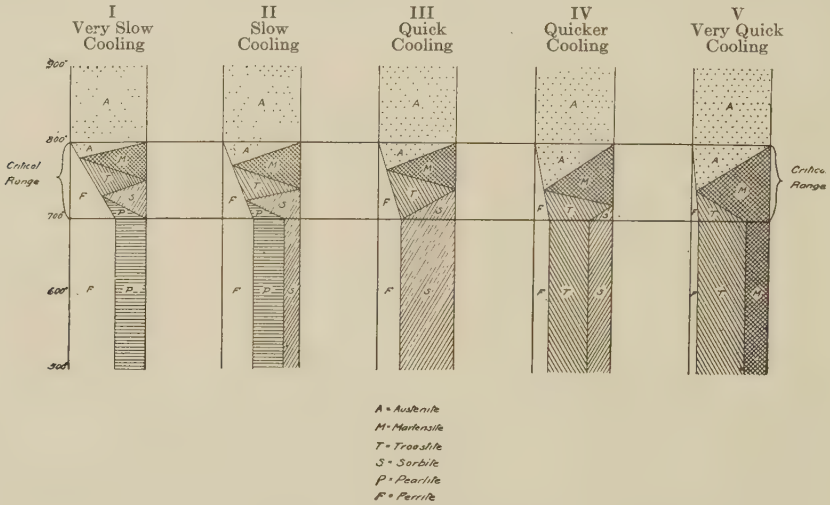


Fig. 159. — Diagram depicting the influence of the rate of cooling on the mechanism of the structural transformation taking place in the critical range in steel containing 0.30 per cent carbon.

transition constituents being formed, namely martensite, troostite, and sorbite. Sorbite has already been described while the nature of martensite and troostite will be discussed in the next chapters. It follows, as indicated in Figure 158, that various types of structures are produced, theoretically at least, while steel cools through its critical range, containing besides free ferrite either (1) austenite and martensite, (2) martensite alone, (3) martensite and troostite, (4) troostite alone, (5) troostite and sorbite, (6) sorbite alone, or (7) sorbite and pearlite.

In Figure 159 it is intended to depict the possibility of retaining in the cold, through suitable regulation of the cooling, these various structures and, therefore, the possibility by this means of imparting to steel many different physical properties. As cooling is accelerated, first some sorbite is retained together with pearlite, then in succession, sorbite alone, sorbite and troostite, etc., while the amount of free ferrite separating decreases. The metal, therefore, becomes stronger, harder, and less ductile (1) because of a diminishing proportion of soft, ductile ferrite and (2) because of tenacious but moderately ductile sorbite replacing weaker but more ductile pearlite. The presence of troostite and martensite is an indication that the metal has cooled so quickly through its critical range that it is hardened, or at least partially so, as explained in Chapter XIV. If the metal is needed in a softer condition it should then be reheated, as explained in the foregoing pages, to slightly below its critical range in

order that the troostite and martensite may be converted into sorbite (a tempering process as explained in Chapter XV.)

It is held by some that when steel is transformed from an austenitic into a pearlitic condition it does not necessarily assume the intermediate forms known as martensite, troostite, and sorbite, the contention being that the *nature of the transformation depends upon the temperature at which it takes place.* Very slow cooling, for instance, which induces transformation at a high temperature, results in the *direct transformation* of austenite into pearlite; faster cooling, by lowering slightly the transformation temperature, causes austenite to transform into sorbite; faster cooling still through

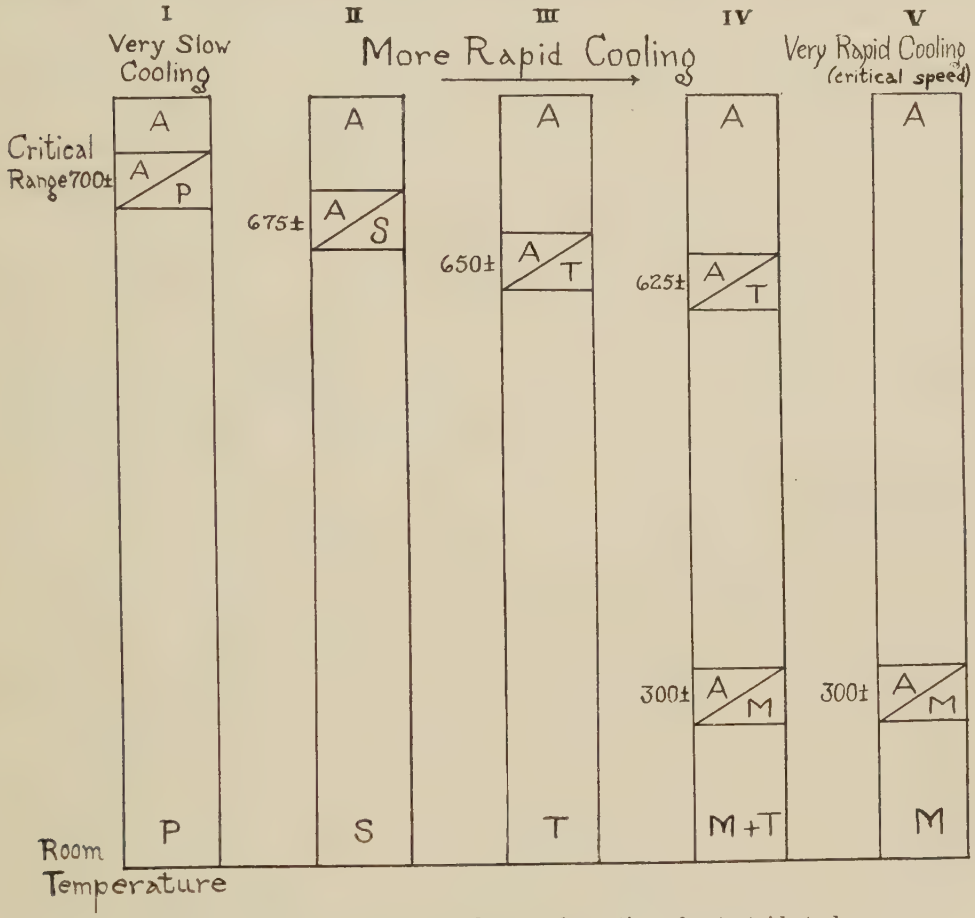


Fig. 160. — Rate of cooling vs. the transformation of eutectoid steel.

further depression of the transformation point results in austenite being converted into troostite; and finally, as later explained, sufficiently fast cooling (the critical speed of quenching), resulting in a *sudden* lowering of the transformation to some 300° C., causes the transformation of austenite into martensite, hence the hardening of the steel. These views are shown graphically in Figure 160. Steel of eutectoid composition has here been selected, there being therefore neither separation of free ferrite nor of free cementite. By comparing this diagram with that of Figure 159 the difference between the two views is clearly brought out. Further light will be

thrown on the mechanisms of the critical transformations of steel in the following chapters devoted to its treatment.

It is somewhat difficult to see how austenite can transform directly into pearlite without first passing through the martensitic state, if our understanding of the nature of martensite is correct. The transformation of the solid solution austenite into the aggregate pearlite implies (1) the allotropic transformation of gamma iron into alpha iron, and (2) the falling out of solution and crystallizing of the carbide Fe_3C. If, as is generally believed, the allotropic transformation of iron *precedes* the crystallization of the carbon, then necessarily before pearlite is formed, a condition must exist where the iron is in the alpha condition and the carbon still in solution, that is the martensitic condition. On further cooling, given the necessary time, the carbide comes out of solution in an extremely fine state of division (colloidal?), troostite being formed, and this is followed by further coagulation of the cementite particles giving rise to the constituent sorbite, and finally by the cementite forming sharply defined lamellæ embedded in a ferrite matrix, resulting in the formation of pearlite.

The author in Chapter XVI offers another possible explanation of the nature of martensite and troostite. The views referred to here are those generally held.

It follows from the foregoing considerations that steel may be, at will, chiefly through suitable regulation of the speed of cooling from the austenitic condition to room temperature, converted into pearlite, sorbite, troostite, or martensite, or into aggregates of two of these constituents, and thus made to acquire widely different physical properties. The various heat treatments applied for such purposes are generally described as annealing, normalizing, hardening, tempering, and drawing. They might properly be referred to as softening, strengthening, and hardening treatments, terms which would be more descriptive of the aims sought. Again softening treatments might be referred to as pearlitizing, hardening treatments, as martensitizing and strengthening treatments, as sorbitizing, or troostitizing, as will be made evident in the following pages. These various treatments may now be considered at greater length.

Hardness of Microscopical Constituents. — Boynton, in the author's laboratory, determined the relative hardness of the various microscopical constituents of steel by means of the Jaggar microsclerometer and obtained the following results:

Constituent	Tested in	Hardness Number
Ferrite	Electrolytic iron	1
	Electrolytic iron, quenched	2.15
	Wrought iron	1.5– 3.6
Pearlite	Steel with 0.13–1.52 per cent C.	1.8– 10.3
	Steel with 0.35–0.86 per cent C.	3.8– 4.2
Sorbite	Steel with 0.48–0.58 per cent C.	5.2– 53.6
Troostite	Steel with 0.58 per cent C.	88.2
Martensite	Steel with 0.20–1.52 per cent C.	38.9–261.6
Austenite	White cast iron with 3.24 per cent C.	103.4
Cementite	Grey cast iron with 3.24 per cent C.	272.8

Grain Size vs. Physical Properties. — The finer the grains, generally the better the physical properties of the steel, this being especially true in regard to resistance to impact, and probably also to fatigue stresses. Portevin writes that steel coarsened by overheating may retain the tensile properties unimpaired but that its resistance to impact will be enormously reduced. As an instance, he mentions two samples of steel, one properly annealed and fine-grained, the other with large grains caused by overheating, which although having identical tensile properties (tensile strength, elastic limit, elongation, and reduction), had impact resistance, by the Charpy test, respectively of 44 and 3 kilogrammeters per cubic centimeter. Brittleness is also increased by the Widmanstätten type of structure. Carbonless iron may be markedly embrittled by coarseness of grains while retaining its ductility under tensile testing.

These considerations point to the unsatisfactory character of the tensile test as the one upon which to base rejection or acceptance of engineering materials. While it may detect brittleness resulting from defective chemical composition, it will not generally reveal brittleness caused by a coarse structure, and will therefore permit the use of steel articles liable to break in service when subjected to shocks. Microscopical examination should be resorted to, and fine-grain structures insisted upon.

It has already been pointed out that the macrostructure of steel should be examined as well as its microstructure.

Maximum resistance to shock, as later explained, is generally obtained after quenching followed by reheating to some 650 deg. C., from which, in the case of carbon steel at least, the metal may be again quenched or slowly cooled. Such treatment results in the production of a very fine sorbitic grain.

CHAPTER XIII

ANNEALING AND NORMALIZING

The aims sought in annealing are generally (1) softness, (2) ductility, and (3) release of strains through (*a*) formation of pearlite, (*b*) grain refinement, and (*c*) uniformity of grain size resulting from suitable heat treatment. From the general considerations outlined in the preceding chapter, it will be evident that in order to

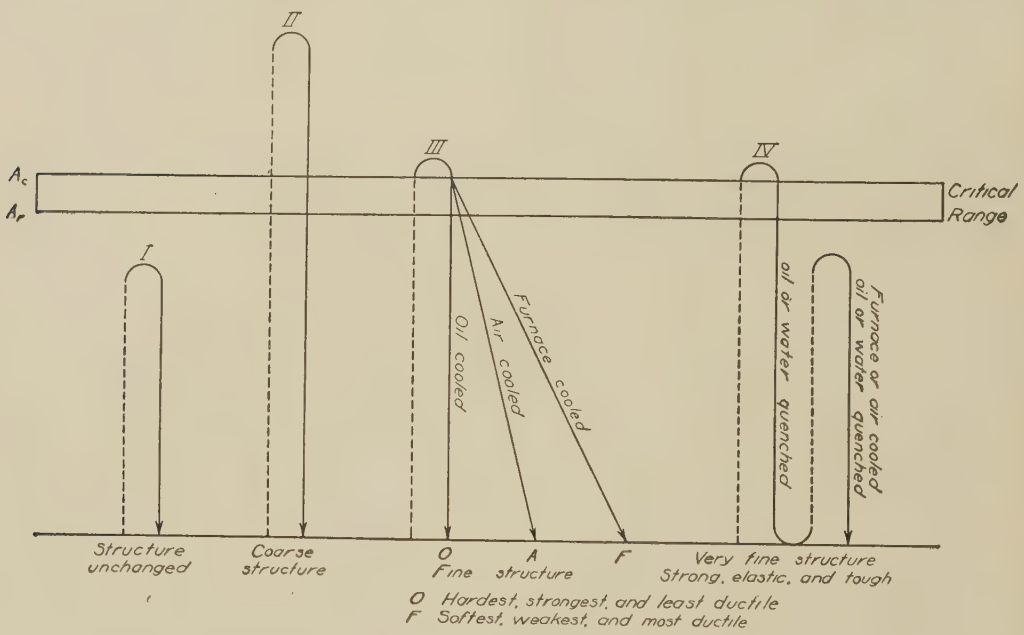


Fig. 161. — Diagram depicting the annealing of steel.

obtain these results, the steel should be made pearlitic. Annealing, therefore, is essentially a pearlitizing treatment and necessarily involves slow cooling from a temperature exceeding the thermal critical range. Steel already in a pearlitic condition but coarse-grained may be improved by annealing because of the finer and more uniform grain which may be imparted to it by that operation. Annealing, moreover, removes existing internal strains as well as the deformation resulting from cold working.

The annealing operation comprises three distinct steps: (1) heating the steel, (2) keeping its temperature constant at the annealing temperature, and (3) cooling it from the annealing to room temperature. These steps will be considered separately.

Heating for Annealing. — The first step in annealing always consists in heating the metal past its critical range so that on subsequent slow cooling it may become

pearlitic and, if the conditions are right, fine-grained. The annealing of steel castings constitutes an apparent exception to the rule that heating just through the range is sufficient to break up effectively the preëxisting structure, for their successful annealing often requires a materially higher temperature or prolonged heating slightly above the range. Should the temperature of the steel remain below its critical range, no structural change would take place and the annealing would be ineffective (I, Fig. 161) unless, indeed, in the case of cold worked hypo-eutectoid steel, when the distorted ferrite may be restored to its normal crystalline structure by heating below the critical range, as later explained.[1] Should, on the contrary, the temperature of the steel be carried considerably above the range, its structure, which was finest as it emerged from the range, begins to coarsen on further heating and continues to grow as the metal cools slowly to the range, so that its final structure would

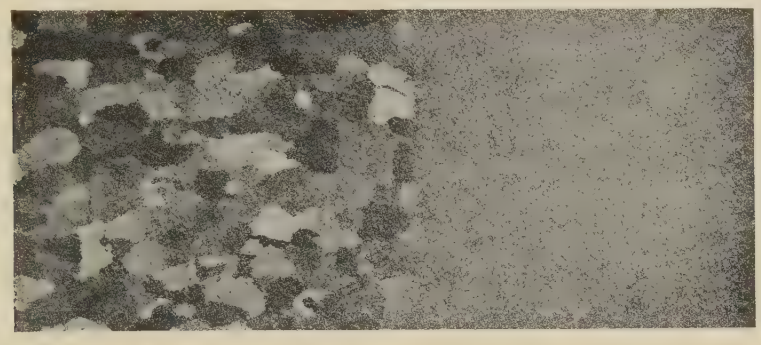


Fig. 162. — Coarsely crystallized soft steel heated at one end to above 900 deg. C. (Stead.)

be at least relatively coarse (II, Fig. 161). Clearly, therefore, to anneal steel forgings they should be heated through their critical range and kept at a temperature as close to the upper part of that range as possible (III, Fig. 161). The annealing temperature will, of course, vary with the carbon content since the position of the critical range, or rather its width, varies likewise. The structural refining taking place in heating through the critical range is strikingly illustrated by Stead in Figure 162, which shows coarsely crystalline soft steel heated at one end to above 900 deg. C. The refined portion was heated above the critical range. The sharp demarcation between the original coarse structure and the fine structure produced by annealing should be noted.

The following ranges of temperatures are recommended by the Committee on Heat Treatment of the American Society for Testing Materials. The report of the committee states that for steels containing more than 0.75 per cent manganese slightly lower temperatures suffice.

Range of Carbon Content	Range of Annealing Temperature
Less than 0.12 per cent	875 to 925 deg. C. (1607–1697 deg. F.)
0.12 to 0.29 per cent	840 to 870 deg. C. (1544–1598 deg. F.)
0. 30 to 0.49 per cent	815 to 840 deg. C. (1499–1544 deg. F.)
0.50 to 1.00 per cent	790 to 815 deg. C. (1454–1499 deg. F.)

[1] When steel contains hardening carbon, it may be softened and made more ductile by heating it to temperatures lower than its critical range (as in the tempering of hardened steel), but such treatment is not, or at least should not be, called annealing. Cooling strains may also be removed, at least in part, by heating below the range.

The proper temperatures to which to heat carbon steels of ordinary commercial quality for the purpose of annealing as well as of hardening are indicated graphically in Figure 163 for various percentages of carbon.

Time Needed to Heat Steel to Furnace Temperature. — Portevin brings out the interesting and, at first, surprising fact that placing steel samples of equal size and form in furnaces heated to different temperatures the sample in the hottest furnace will reach its temperature in a *shorter* time than the sample placed in the colder furnace. A steel cylinder, for instance, measuring 30 mm. in diameter, placed in a furnace heated to 1000 deg. C. reached that temperature in 9 minutes, while it required 12 minutes for a similar sample placed in a furnace heated to 800 deg. C. to reach that

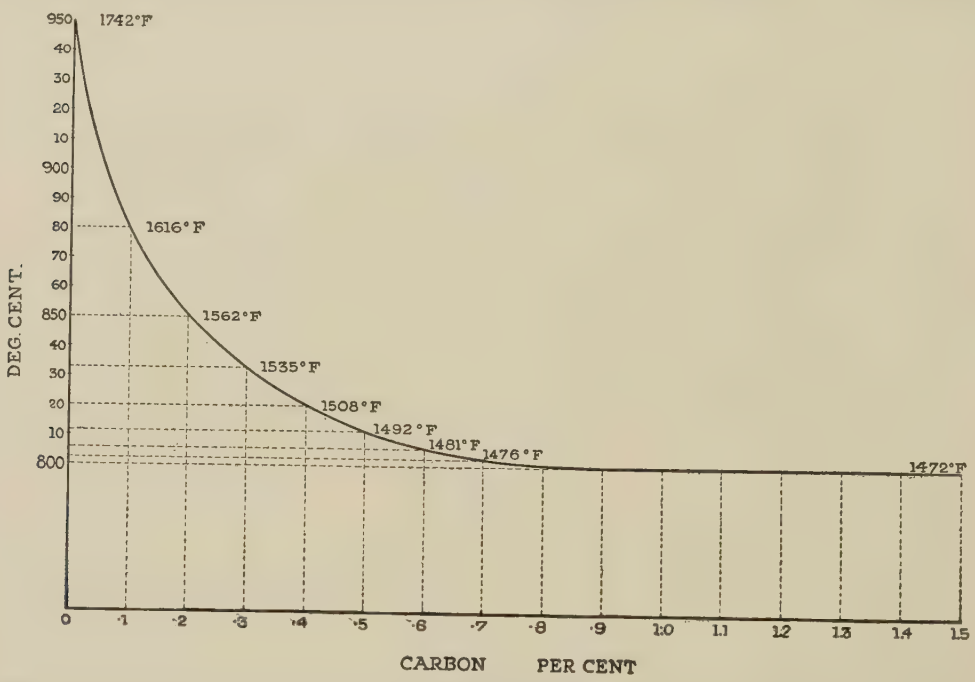


Fig. 163. — Diagram showing suitable temperatures for annealing (and hardening) carbon steel forgings.

temperature. The following diagram (Fig. 164) may help in explaining this phenomenon. The piece placed cold in a furnace heated to 1000 deg. C. will increase in temperature more rapidly than the piece placed in the furnace heated to 800 deg. C. because of the greater difference between the temperature of that piece and the surrounding furnace walls, the radiations being proportional to the difference between the fourth powers of their respective absolute temperatures. We may represent the respective velocities of heating at the start by A B and A′ B′. The sample in the hotter furnace will necessarily reach a temperature of 800 deg. C. before that temperature is reached by the sample placed in the colder furnace. We may assume that by the time the former piece is heated to 800 deg. C. the temperature of the latter is but 600 deg. The rate of heating of the first piece may then be represented by C D greater than C′ D′, representing the speed of heating of the second piece, from which it follows that the first piece will reach its final temperature of 1000 deg. before the other attains its final temperature of 800 deg.

An apparent exception to this rule is observed when a piece of steel is placed in a furnace the temperature of which is but slightly above the critical point of the metal, when it will be found that the time required is abnormally long. This is readily accounted for by the absorption of heat occurring at the critical point, which the slightly higher temperature of the furnace is necessarily very slow in overcoming.

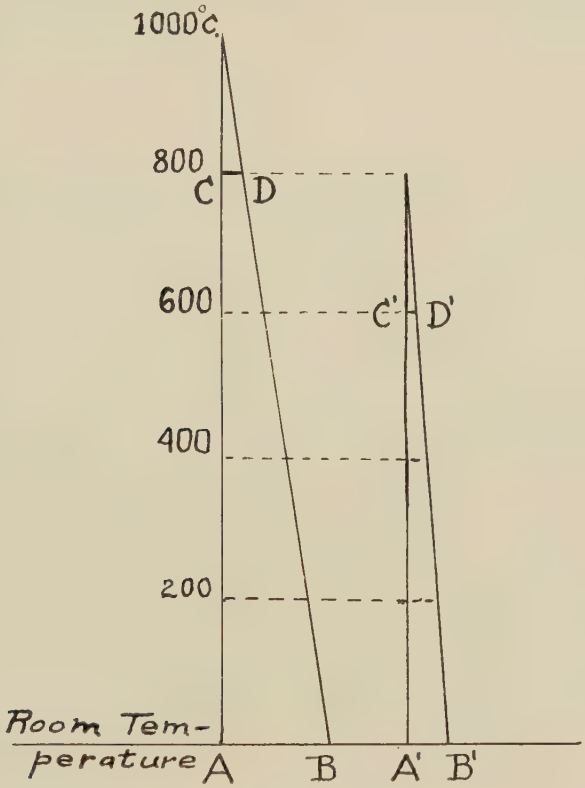


Fig. 164. — Speed of heating vs. furnace temperature.

In a hotter furnace the same absorption of heat occurs but is much more rapidly overcome, the sample soon resuming its normal rate of heating.

Portevin gives the following formula for the time required for heating pieces of various diameters respectively to 800 and 1000 deg. C., the pieces being placed, cold, in furnaces maintained at constant temperature:

$$Z = 4\,d \quad \text{— for 800 deg. C.}$$
$$Z = 3\,d \quad \text{— for 1000 deg. C.}$$

in which d represents the diameter in centimeters, and Z the time in minutes.

Assuming, for instance, a cylinder measuring 12 inches in diameter, or 30 cms., the time required for heating respectively to 800 and 1000 deg. C. in furnaces maintained at these temperatures will be:

$$Z = 4 \times 30 = 120 \text{ min.} = 2 \text{ hrs. for heating to 800 deg. C.}$$
$$Z = 3 \times 30 = 90 \text{ min.} = 1\tfrac{1}{2} \text{ hrs. for heating to 1000 deg. C.}$$

Time at Annealing Temperature. — The steel object should be kept at the annealing temperature long enough to be heated right through to that temperature.

The Committee on Heat Treatment, referred to above, states that an exposure of one hour should be long enough for pieces twelve inches thick. Thicker pieces, of course, need a longer heating.

Cooling from Annealing Temperature. — Having imparted a fine structure to the steel the next step must be to retain it. The most effective way of accomplishing this consists in cooling the steel very quickly, by quenching it in water for instance, as time is then denied for the structure to coarsen at all while the metal cools to room temperature. Such rapid cooling, however, as is well known, hardens the metal and deprives it of ductility (unless, indeed, it contains very little carbon), and this would defeat the purpose of annealing, which always demands the retention of considerable ductility. To obtain maximum softness and ductility the steel should be made pearlitic, hence cooled very slowly, to wit, with the furnace in which it was

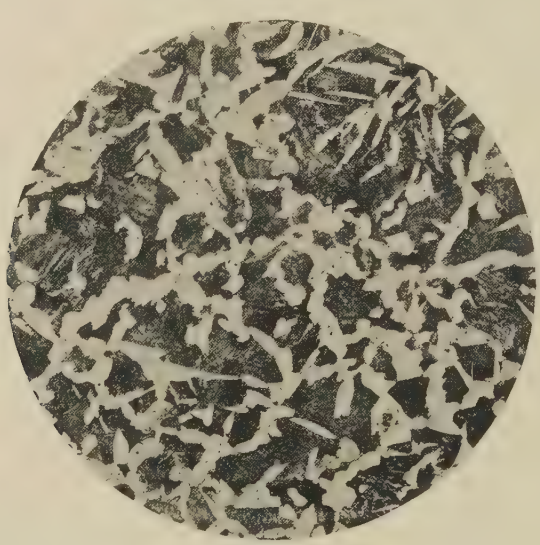


Fig. 165. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and slowly cooled in furnace. (R. W. Smyth, in the author's laboratory.)

heated.[1] If greater hardness (for wearing power), strength, and elasticity are desired, at the necessary sacrifice of some ductility, the cooling should be more rapid, as, for example, in air. (See Normalizing.)

Rate of Cooling vs. Carbon Content. — The lower the carbon content the more rapid may be the cooling from the annealing temperature without affecting too deeply the ductility of the metal. For instance, (1) steel containing not over 0.15 per cent carbon may be quenched in water, thereby increasing its strength and elastic limit and still remain very ductile, (2) steel with less than 0.20 per cent carbon may be quenched in oil with satisfactory results, (3) with a larger proportion of carbon such rapid cooling is no longer possible, as it would destroy the ductility of the metal, recourse having then to be had to cooling in air for the desired combination of strength and ductility or to the double annealing treatment soon to be described. It may be contended, however, that any treatment which fails to make the steel pearlitic should

[1] Unless the double treatment presently to be described is resorted to.

not be called annealing. With this in mind, cooling from the annealing temperature must necessarily be very slow.

Rate of Cooling vs. Size of Object. — Since large objects necessarily cool more slowly than smaller ones when subjected to the same cooling influences, it is evident that the external conditions should also be regulated in accordance with the dimensions of the objects treated. To secure maximum softness and ductility, for instance, the cooling of small objects should be more effectively retarded than the cooling of larger ones. Assume, for example, two objects made of the same steel, one large and one small, and both cooled in air from the annealing temperature; the smaller object will be harder and less ductile than the larger one, because of its quicker cooling. To

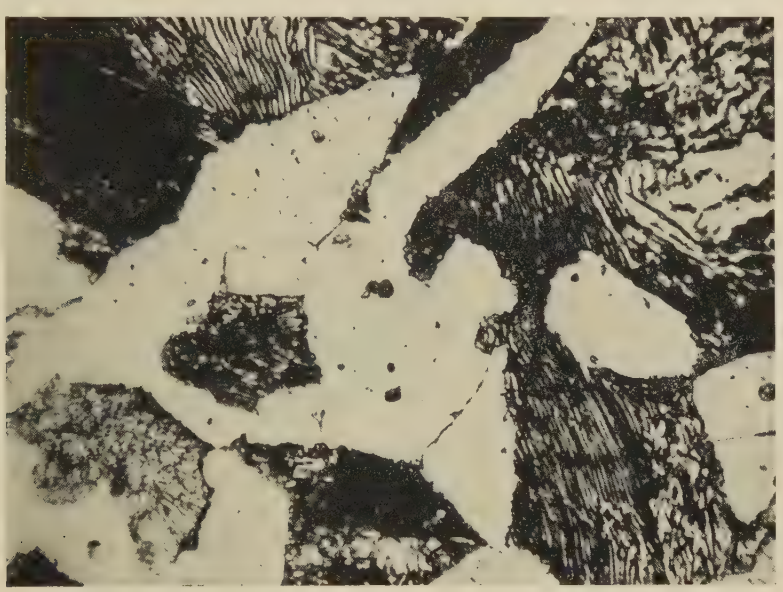


Fig. 166. — Steel. Carbon 0.50 per cent. Magnified 670 diameters. Heated to 1000 deg. C. and slowly cooled in furnace. (C. C. Buck, Correspondence Course student.)

render it as soft and ductile as the larger object, cooling in the furnace may be necessary. Similarly, to give strength and high elastic limit the cooling of large objects must be more vigorously hastened than that of smaller objects, as, for instance, cooling in oil against cooling in air for the smaller piece.

Furnace Cooling from Annealing Temperature. — As an example of the effect of furnace cooling upon the structure of steel, let us take a steel bar ½ inch square, containing 0.50 per cent carbon, heated to 1000 deg. C. and slowly cooled with the furnace. Its structure is shown in Figures 165 and 166. It will be seen to be composed of the normal proportions of pearlite and free ferrite, namely some 60 per cent of the former, and it will also be noted that the pearlite is distinctly laminated (Fig. 166), and that in places at least the ferrite forms characteristic polyhedral grains. This structure is due to the slow cooling of the steel through its critical range, which permits the rejection of the full amount of free ferrite and a distinct crystallization of the constituents of the residual austenite into plates of ferrite and cementite. The relative softness and great ductility of the steel in this condition is due (1) to the

presence of the full amount of soft ferrite in relatively large areas and (2) to the presence of distinctly laminated pearlite, indicating the absence of hardening carbon, as explained later.

Normalizing. — Air cooling from a temperature exceeding the critical range is generally referred to as "normalizing." Tiemann describes normalizing as follows: "A form of annealing known as normalizing consists in reheating to a temperature above the critical range, holding at that temperature a certain length of time, and then cooling in air; it is commercially used to secure uniform conditions on materials treated in various ways or where, as in the case of billets, the finishing temperature and amount of hot working have resulted in a very coarse grain; this term was sug-

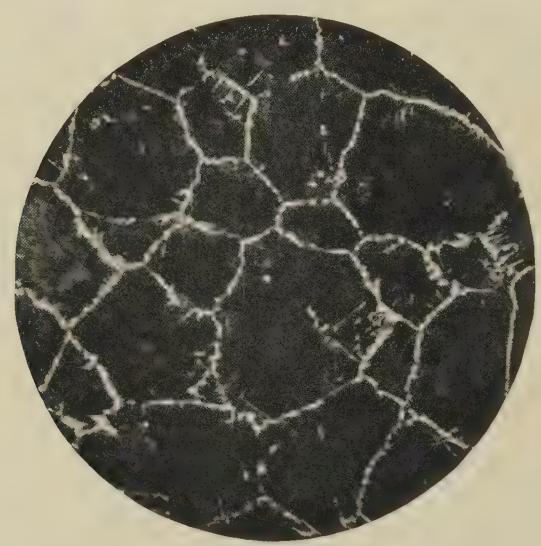


Fig. 167. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and cooled in air. (Boynton, in the author's laboratory.)

gested by Arnold, and *equalizing* was suggested by Stead as more suitable but has not come into any extended employment."

It is evident that such treatment may result in the formation of pearlite if the piece is sufficiently large, while it may result in the formation of sorbite or of an aggregate of sorbite and pearlite in pieces of small cross section because of their more rapid cooling. It is an error to assume, therefore, that normalizing imparts identical structural conditions to all steels regardless of the dimensions of the pieces treated, and this should be borne in mind when considering the physical properties of different steels in the "normalized" condition. Unless the samples submitted to normalizing for purposes of comparison are of identical dimensions, the results will not be comparable.

It might also be added that when comparing steels of different chemical compositions, unless they have been cast under identical conditions into ingots of equal size and submitted to the same amount of reduction by work, the results after normalizing or any other heat treatment will not constitute a fair test of their relative qualities. Failing to bear this in mind may lead us, as it too frequently does, to com-

pare a steel with large original dendrites, for instance, and intensely reduced by work, with one with small dendrites and but slightly reduced and to classify them in an order which might be reversed had we endeavored first to impart to them like macrostructures.

To illustrate the influence of air cooling upon the structure of steel, let us take a small bar of steel containing some 0.50 per cent carbon, heated to 1000 deg. C. and cooled in air. Its structure is shown in Figure 167. It will be found quite unlike the structure of the same steel after furnace cooling (Figs. 165 and 166). It contains a much smaller proportion of free ferrite, apparently not over 20 per cent, in the form of a distinct net surrounding dark meshes which a high magnification fails to

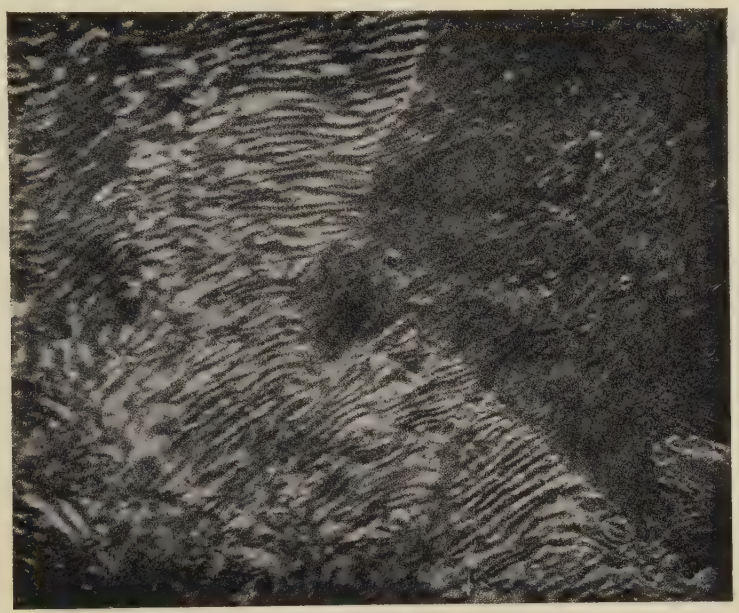


Fig. 168. — Steel. Carbon 1 per cent. Magnified 1500 diameters. Pearlite (laminated) passing into sorbite. (Osmond.)

resolve into distinct parallel plates. Relatively quick cooling through the critical range has prevented the separation of the normal amount of free ferrite, from which it necessarily follows that the dark constituent contains more ferrite than true pearlite; nor has it the structure of true pearlite, time also having been denied on cooling through the range for the formation of distinct plates of ferrite and cementite. Sorbite is the name of this constituent. The structure of pearlite passing into sorbite is shown in Figure 168.

Properties of Sorbite. — Sorbite can be produced in steel forgings of small sections through simple air cooling from a finishing temperature or from a reheating temperature superior to the critical range, and in larger sections by hastening somewhat their cooling through that range. It has been stated that sorbite is harder, stronger, and less ductile than pearlite. By so regulating the cooling from the annealing temperature, therefore, that sorbitic steel is produced, hardness, strength, and elasticity will be promoted at the sacrifice of some ductility (III, Fig. 161).

Influence of Maximum Temperature. — The influence of the maximum tem-

perature to which steel is heated before being allowed to cool is well shown in Figures 169–170, which should be compared with Figures 165 and 166. The constituents are the same, namely, ferrite and pearlite, but the higher temperature resulted in the formation of larger particles, evidently because of the formation above the critical range of larger austenitic grains.

Fig. 169. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 800 deg. C. and cooled in furnace. (C. C. Buck, Correspondence Course student.)

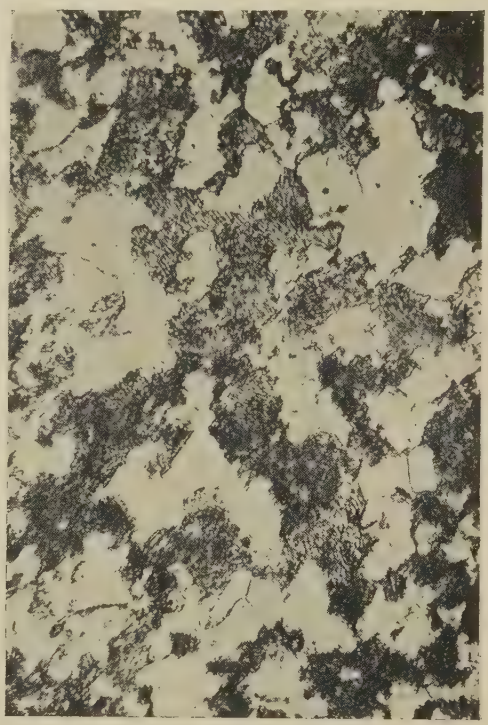


Fig. 170. — Steel. Carbon 0.50 per cent. Magnified 670 diameters. Heated to 800 deg.C. and slowly cooled in furnace. (C. C. Buck, Correspondence Course student.)

Influence of Time at Maximum Temperature. — Maintaining steel for a long time at a high temperature causes the formation of large austenite grains, which in passing through the range are converted into large pearlite or sorbite grains with rejection of free ferrite in hypo-eutectoid steel and of free cementite in hyper-eutectoid steel. It is also noted that the more prolonged the heating the smaller the amount of the excess constituent (free ferrite or free cementite) separating on rapid (air) cooling through the range. This is shown in Figure 171, in which is depicted the structure of steel containing 0.50 per cent carbon heated to 1150 deg C. for two hours and air cooled. The very large sorbitic grains should be noted as well as the very small proportion of free ferrite.

Oil and Water Quenching from Annealing Temperature. — As already explained, only steel containing very little carbon may be quenched in oil or water if much ductility is to be retained, unless, indeed, the double treatment soon to be described be employed, when higher carbon steels may be so quenched. The structure of steel containing 0.10 per cent carbon, heated to 950 deg. C. and quenched in water, is

shown in Figure 172, while in Figure 173 is seen the structure of steel containing 0.20 per cent carbon quenched in oil from a temperature of 850 deg. C. Rapid cooling through the range did not prevent the separation of much of the large amount of excess ferrite present in these steels, hence their softness and ductility even after quenching. They are, however, somewhat stronger and have higher elastic limit than similar steels more slowly cooled, (1) because they contain a somewhat smaller proportion of soft free ferrite, (2) because the free ferrite they contain has crystallized into smaller grains, and (3) because their carburized constituent is sorbitic or even martensitic rather than pearlitic.

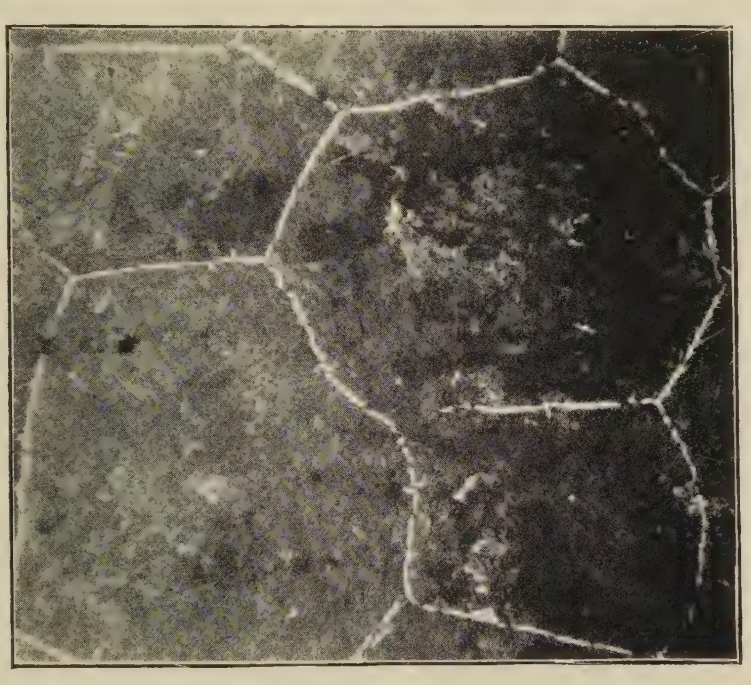


Fig. 171. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1150 deg. C. for two hours and cooled in air. (Boynton, in the author's laboratory.)

Annealing Eutectoid Steel. — While the mechanism of the structural changes taking place on annealing steel has been made clear in the preceding pages, it may not be without interest to consider further and in succession the annealing of eutectoid, hypo-euctecoid, and hyper-eutectoid steel, as these three types of steels have different structures and their annealing involves different structural changes.

Eutectoid steel, upon being heated through its single critical point, namely $Ac_{3\cdot2\cdot1}$, is converted into a solid solution (austenite). The grains of this austenite are very fine as the steel emerges from its range and they are kept from growing by preventing the steel from reaching a higher temperature. On cooling through $Ar_{3\cdot2\cdot1}$ the metal becomes pearlitic if it be given time, as for instance in cooling in the furnace, while it becomes sorbitic if cooled more quickly, as for instance in air in the case of small objects.

It has been explained in Chapter X that, for like treatments, the structure of

eutectoid steel is finer than that of either hypo-eutectoid or hyper-eutectoid steel, and this holds true in the case of annealed samples, although the difference may not be

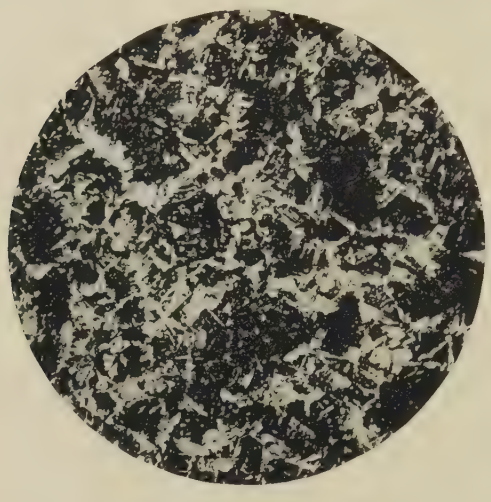


Fig. 172. — Steel. Carbon 0.10 per cent. Magnified 100 diameters. Heated to 950 deg. C. and quenched in water. (Boylston.)

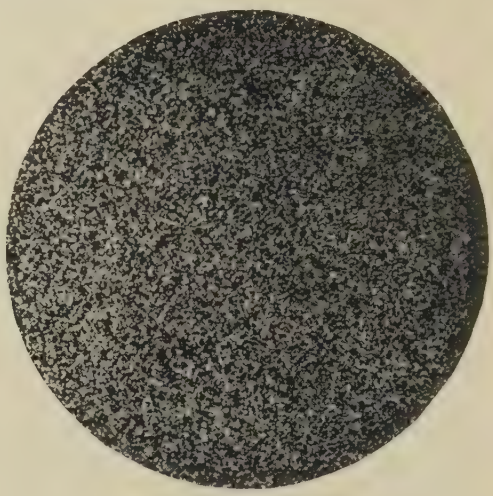


Fig. 173. — Steel. Carbon 0.20 per cent. Magnified 100 diameters. Heated to 850 deg. C. and quenched in oil. (Boylston.)

Fig. 174. — Steel, eutectoid. Magnified 412 diameters. Heated to 800 deg. C. and slowly cooled in furnace. (C. C. Buck, Correspondence Course student.)

noticeable when comparing the structure of eutectoid steel with that of hyper-eutectoid steel containing but a slight excess of free cementite.

In Figure 174 is shown the structure of eutectoid steel heated to 800 deg. C. and slowly cooled in the furnace. It is made up of well-developed pearlite.

Annealing Hypo-Eutectoid Steel. — Slowly cooled hypo-eutectoid steel is an aggregate of pearlite and free ferrite. On being heated through its critical range, as soon as the point Ac_1 is reached, the pearlite is bodily converted into austenite, while the ferrite still remains free. On further heating, however, it begins to be absorbed by austenite, its absorption being completed as the metal emerges from its Ac_3 point. Above Ac_3 the steel is composed wholly of homogeneous austenite. On cooling through the critical range — unless, indeed, the cooling be very rapid and sufficient carbon be present — ferrite is again liberated in amount proportional to the slowness of the cooling up to the maximum quantity consistent with the carbon content in

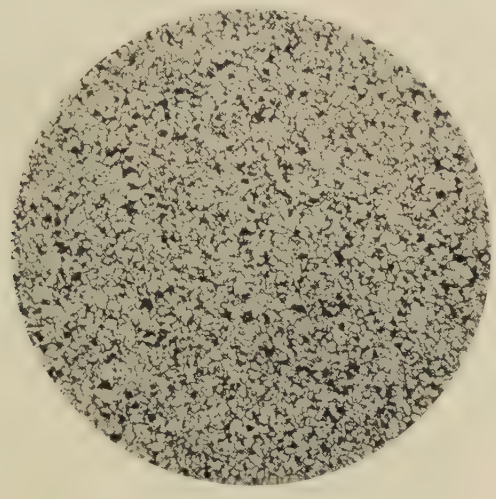


Fig. 175. — Steel, hypo-eutectoid. 0.20 per cent carbon. Annealed. Magnified 100 diameters. (W. J. Burger, Correspondence Course student.)

the steel. If the cooling be very slow then, for instance in the furnace, the totality of the excess ferrite will be rejected and the residual austenite converted into well-defined pearlite (Fig. 166), while if the cooling be more rapid, for instance in air in the case of small objects, a portion only of the excess ferrite is liberated while the residual austenite is converted into sorbite (Fig. 167). The liberation of ferrite taking place during the slow cooling of hypo-eutectoid steel coarsens its structure and is the chief reason why annealed hypo-eutectoid steel cannot have so fine a structure as annealed eutectoid steel. Howe further contends that as hypo-eutectoid steel is heated from Ac_1 to Ac_3 a new crystalline growth takes place which is the coarser the greater the distance between A_1 and A_3, that is the less carbon in the steel, so that by the time the old structure has been obliterated, i.e. at Ac_3, a new grain has formed, which is an additional reason why the structure of hypo-eutectoid steel cannot be refined to the same extent as that of eutectoid steel.

An additional illustration of the fine structure that can be imparted to hypo-eutectoid steel by annealing is given in Figure 175 in the case of steel containing 0.20 per cent carbon.

Annealing Hyper-Euctectoid Steel. — Slowly cooled hyper-eutectoid steel is an aggregate of pearlite and free cementite. On heating it through its critical range, i.e.

through its $Ac_{3\cdot2\cdot1}$ and Ac_{cm} points, pearlite is converted into austenite at the lower point and this austenite absorbs the free cementite as the metal is further heated from $Ac_{3\cdot2\cdot1}$ to Ac_{cm}. At Ac_{cm} the absorption is complete and the metal composed entirely of austenite. On cooling through the range, if time be given, as for instance in cooling in the furnace, the full proportion of free cementite is again liberated and the residual austenite converted at $Ar_{3\cdot2\cdot1}$ into clearly laminated pearlite (Fig. 176). If the cooling be more rapid, as for instance in cooling small pieces in air, a portion only of the free cementite is set free, while the residual austenite is converted into sorbite. This setting free of cementite, like the liberation of ferrite in hypo-eutectoid steel, coarsens the structure. The coarsening influence of free cementite, however, is far from being as marked as that of free ferrite, chiefly because free cementite

Fig. 176. — Steel 1.40 per cent carbon. Annealed. Magnified 600 diameters. (E. L. Reed, in the author's laboratory.)

is generally present in much smaller proportions. Steel containing as much as 1.50 per cent carbon, for instance, contains but 11.00 per cent of coarsening cementite, while steel with 0.40 carbon contains 53.2 per cent of coarsening ferrite.

For the purpose of annealing hyper-eutectoid steel, it is seldom advisable to heat it much above its lower critical point $Ac_{3\cdot2\cdot1}$, because while at Ac_{cm} the free cementite would be completely reabsorbed and, through relatively quick cooling, could be prevented, to a certain extent at least, from again separating, the coarseness of structure resulting from so high a temperature would generally more than offset the gain resulting from the presence of a smaller proportion of free cementite.

Annealing of Cold Worked Steel. — It has already been mentioned that the cold working of steel, that is, the application of severe compression or tension when its temperature is below its critical range, and more specifically at room temperature, results in a marked distortion of its structural elements, a decided elongation for instance if the steel is subjected to tension as in wire drawing (Fig. 177, also Figs. 152 and 153, Chapter XI), and that such distortion causes a great increase of tenacity and hardness but that it lowers the ductility decidedly, eventually producing brittle-

ness. It has also been stated that many other properties of steel are deeply affected and that this action of cold working is ascribed by some to the formation of a certain amount of amorphous iron (Chapter XI).

When it is desired to increase the ductility of cold worked steel in order that it may be subjected to additional drafting or because the uses to which it is to be put call for greater ductility and softness, the metals should be subjected to suitable heat treatment. In the case of cold worked hypo-eutectoid steel which is composed of elongated particles of ferrite and pearlite it is sufficient in order to increase its duc-

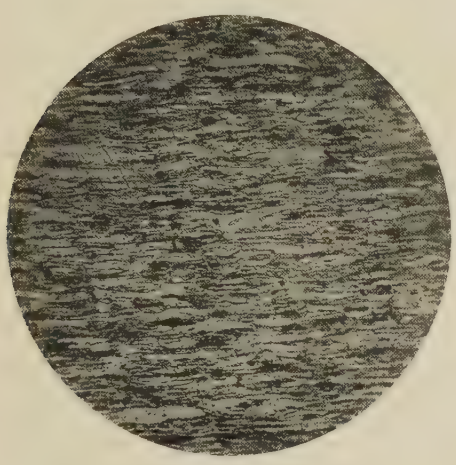


Fig. 177. — Steel wire. 0.08 per cent carbon. Cold drawn. Magnified 100 diameters. (E. H. Peirce.)

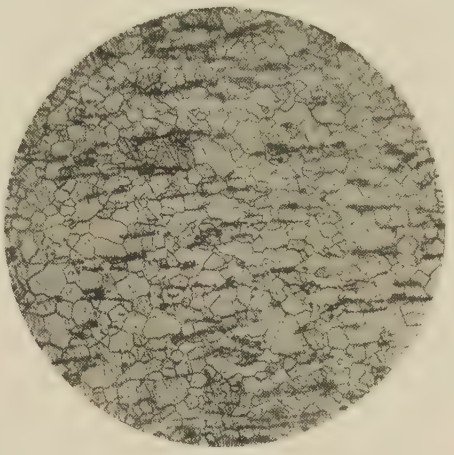


Fig. 178. — Steel wire. 0.08 per cent carbon. Cold drawn and reheated below its critical range. Magnified 100 diameters. (E. H. Peirce.)

tility materially to heat it to a temperature varying between 550 and 600 deg. C. and, therefore, considerably below its critical range (see Fig. 178). This is especially so when the carbon content does not exceed 0.40 per cent and when therefore the metal contains a large amount of free ferrite. It has been stated by some that 520 deg. C. marks the temperature which should be reached in order to produce the desired results in very low carbon steel. This heating of cold worked steel below the critical range to increase its ductility is sometimes called at the works "process" or "works" annealing. The treatment causes the free ferrite to recrystallize in its normal polyhedral pattern (Fig. 178) and, if we believe in the existence of amorphous iron in cold worked steel, the return of that amorphous iron to the crystalline condition and hence decreased hardness and strength and increased ductility. It should be noted, however, that the elongated particles of pearlite remain elongated (Fig. 178), the ferrite particles alone being affected by this treatment. When maximum softness is required the cold worked steel must be annealed by heating it above its critical range followed by slow cooling. This treatment, of course, removes the distortion of the pearlite as well as of the ferrite (Fig. 179) since both constituents above the critical range form a homogeneous solid solution. In wire mills this is known as "dead soft" annealing. The recrystallization of deformed ferrite by heating below the thermal critical range, frequently referred to as "grain growth," will be found discussed at greater lengths in Chapter XVII.

When it is desired to produce wires having a very high yield point and very great tenacity (300,000 to 400,000 lbs. per sq. in.) while retaining considerable toughness, the heat treatment is so conducted as to produce sorbite to the practical exclusion of pearlite, free ferrite, or free cementite, and is generally applied to steel wires contain-

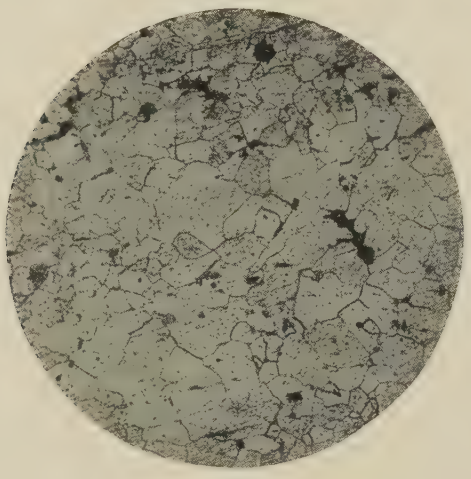


Fig. 179. — Steel wire. Cold drawn and reheated above its critical range. Magnified 100 diameters. (Boylston.)

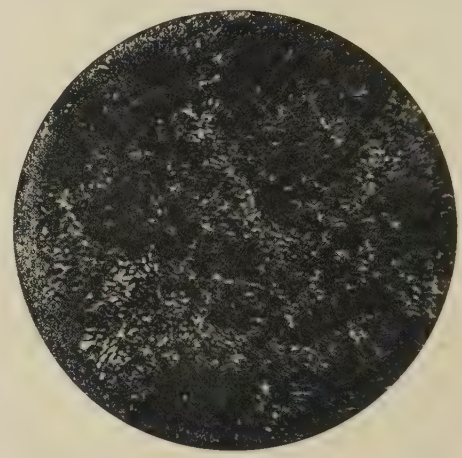


Fig. 180. — Patented steel wire. 0.85 per cent carbon. Magnified 1000 diameters. (E. H. Peirce.)

Fig. 181. — Steel, cast. Carbon 0.30 per cent. Magnified 100 diameters. Annealed. (W. J. Burger, Correspondence Course student.)

ing some 0.35 to 0.85 per cent carbon. The process is known as "patenting" and the product as "patented" wire. To produce sorbite the cooling through the critical range should be relatively rapid but not so rapid as to cause the retention of martensite or even troostite lest the steel be brittle, nor should it be slow enough to permit the formation of pearlite since this would imply decreased tenacity. Patenting in practice is usually conducted as a continuous operation, the wire being led through

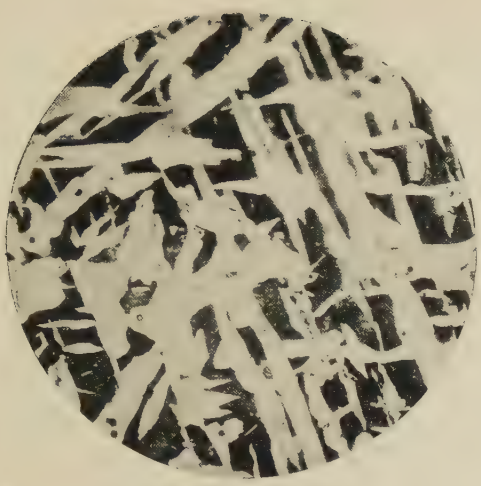


Fig. 182. — Cast condition.

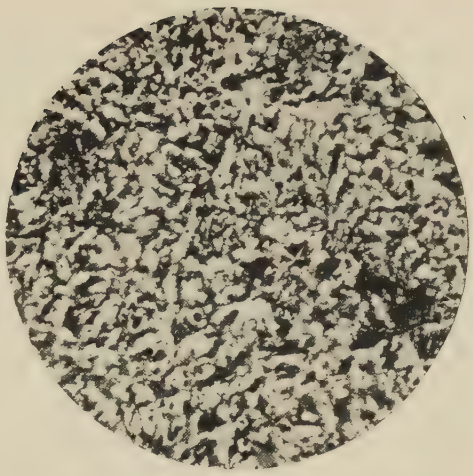


Fig. 183. — Heated to 875 deg. C. and furnace cooled.

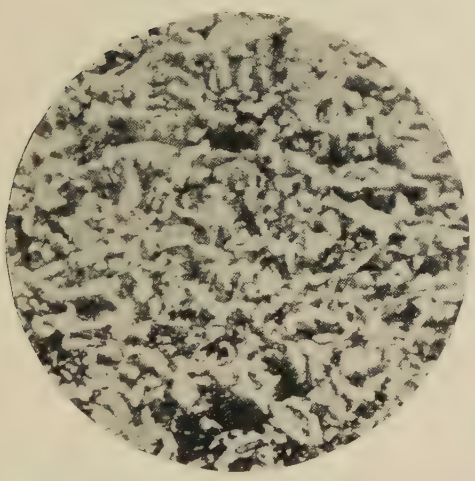


Fig. 184. — Heated to 875 deg. C. for five hours and air cooled.

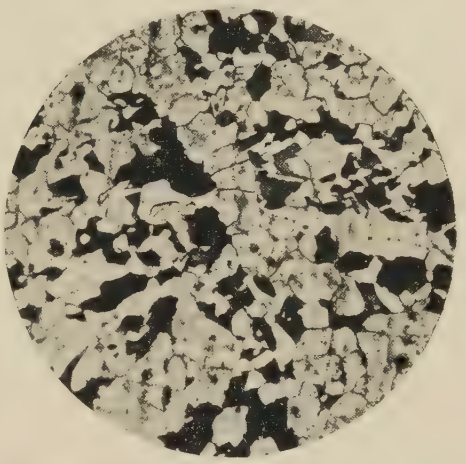


Fig. 185. — Heated to 875 deg. C. and air cooled.

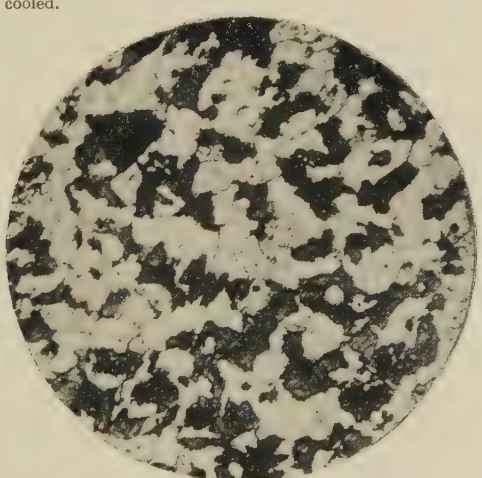


Fig. 186. — Heated to 1100 deg. C. and air cooled, reheated to 875 deg. C. and air cooled.

Annealing of cast steel containing 0.30 per cent carbon. All photomicrographs are magnified 100 diameters. (R. S. Simmons, in the author's laboratory.)

the heated tubes of a furnace and cooled by being brought into the air or into a bath of molten lead comparatively cool but seldom below 700 deg. F. (367 deg. C.). The structure of patented wire is shown in Figure 180.

J. T. Tinsley writes that by a proper combination of drafting and patenting it is possible to obtain music wire from a 0.70 per cent carbon steel which will have a tensile strength of 400,000 lbs. per sq. in., and be sufficiently tough to be wrapped about itself without breaking and be swaged flat to one-half its original thickness without splitting. He also states that although it might at first be supposed that wire annealed to a pearlitic condition because of its greater softness and ductility should withstand drafting to a greater extent than patented (sorbitic) wire, the facts are that owing to the rapid loss of ductility characteristic of a pearlitic structure it will not withstand drawing to anywhere near the same degree as will the patented structure.

Annealing Steel Castings. — It has been mentioned that the very coarse structure of steel castings, called "ingotism" by Howe, was not so readily refined as the structure of steel forgings, its satisfactory annealing often necessitating prolonged heating slightly above the range or short heating to temperatures considerably higher than the critical range. Notwithstanding their greater resistance to the annealing treatment, successfully annealed castings may possess physical properties fairly equal to those of forgings. In Figure 181 is shown the structure of cast steel containing some 0.30 per cent of carbon and properly annealed. When highly magnified the carbon-holding constituent should have a sorbito-pearlitic appearance.

The Committee on Heat Treatment of the American Society for the Testing of Materials recommends, for the purpose of annealing, heating carbon-steel castings slowly and uniformly to temperatures varying with the carbon content of the steel approximately as follows:

Carbon per Cent	Temperatures Deg. C.
Up to 0.40 inclusive	900
0.40 to 0.60 inclusive	850
Over 0.60	830

The castings should be kept at the maximum temperature a sufficient length of time to ensure the refining of the grain. The castings should be cooled (1) slowly and uniformly in the furnace when it is desired that the steel shall possess the maximum softness, and (2) at an accelerated rate when it is desired that the steel possess rather higher tensile strength and elastic limit.

The rather long annealing indicated above may be replaced by heating the castings to some 1200 deg. C. for a few minutes, cooling in the air, and reheating to a temperature slightly above $Ac_{3\cdot2\cdot1}$, $Ac_{3\cdot2}$, or Ac_1 (J. H. Hall).

The structures imparted to cast steel containing 0.30 per cent carbon (Fig. 182) by various annealing treatments are illustrated in Figures 183 to 186.

Structure vs. Heat Treatment. — Some of the many different structures produced by various treatments are shown in a convenient form in Figures 187 and 188 in the case of steels containing respectively 0.30 and 0.50 per cent carbon and otherwise of good commercial quality. The treatments corresponding to each structure are indicated in the accompanying legenda.

Varieties of Pearlite. — From the foregoing it will be evident that several varieties of pearlite are to be considered and that the physical properties of steel will de-

pend greatly upon the character of the pearlite it contains. Arnold considers four varieties which are well illustrated in Figure 189. His first phase, which he calls

Fig. 187. — Various structures of steel containing 0.30 per cent carbon. Magnified about 30 diameters.

Legenda for Figure 187

1. Cast condition.
2. Cast and improperly annealed.
3. Cast and properly annealed.
4. 1½-in. rolled bar heated for 2 hours at 1000 deg. C. and cooled in furnace.
5. ½-in. rolled bar heated to 1000 deg. C. and cooled in furnace.
6. 1½-in. round rolled bar heated to 1000 deg. C. and cooled in furnace.
7. ½-in. round rolled bar heated to 1000 deg. C. and cooled in furnace.
8. ½-in. round rolled bar heated to 900 deg. C. and cooled in furnace.
9. ½-in. round rolled bar heated to 900 deg. C. and cooled in air.
10. ½-in. round rolled bar heated to 900 deg. C. and cooled in oil.
11. ½-in. round rolled bar heated to 900 deg. C. and cooled in water.
12. ½-in. round rolled bar heated to 900 deg. C. and cooled in oil; reheated to 650 deg. C. and cooled in oil.
13. 1½-in. round rolled bar heated to 900 deg. C. and cooled in oil; reheated to 650 deg. C. and cooled in oil.
14. ½-in. round rolled bar finished at proper temperature.
15. 1½-in. round rolled bar finished at high temperature.
16. Cold worked.

"sorbitic" pearlite, is generally called sorbite by other writers. The character and physical properties of sorbite have been described, as well as some of the conditions necessary to its formation. His second and third phases, to which he gives the names respectively of "normal" and "laminated" pearlite, are both true pearlite, the thicker

lamellæ of the latter being due to a slower cooling through the critical range. His fourth phase is pearlite in the process of spheroidizing (see Chapter XVII).

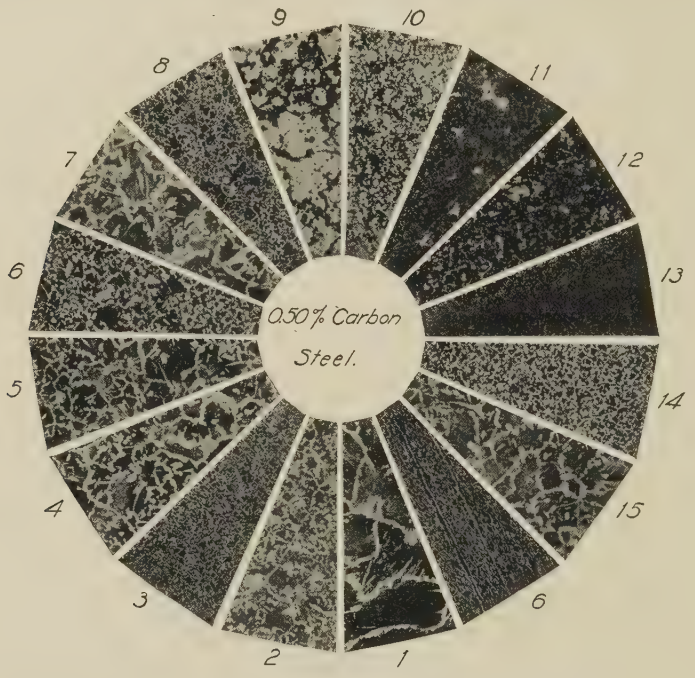


Fig. 188. — Various structures of steel containing 0.50 per cent carbon. Magnified about 30 diameters.

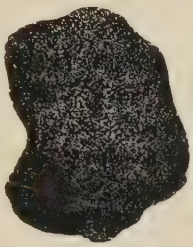
Legenda for Figure 188

1. Cast steel.
2. Cast steel improperly annealed.
3. Cast steel properly annealed.
4. ½-in. round rolled steel cooled from 1100 deg. C. in the furnace.
5. ½-in. round rolled steel cooled from 100 deg. C. in the furnace.
6. ½-in. round rolled steel cooled from 900 deg. C. in the furnace.
7. ½-in. round rolled steel soaked 2 hours at 900 deg. C. and cooled in the furnace.
8. ½-in. round rolled steel cooled from 900 deg. C. in the air.
9. ½-in. round rolled steel cooled from 1000 deg. C. in water.
10. ½-in. round rolled steel cooled from 900 deg. C. in water.
11. ½-in. round rolled steel cooled from 900 deg. C. in oil.
12. ½-in. round rolled steel quenched in water while passing through critical range.
13. ½-in. round rolled steel quenched in oil from 850 deg. C.; reheated to 600 deg. C. and quenched in oil.
14. ½-in. round steel finished at proper temperature.
15. Large forging showing finishing at too high a temperature.
16. Cold worked.

It is now understood that true, i.e. clearly laminated, pearlite only has a constant composition, being in this respect similar to all eutectic and eutectoid alloys as explained in Chapter XXIV. In hypo-eutectoid steel sorbite generally contains more ferrite and, therefore, a smaller percentage of carbon than pearlite, while in hyper-eutectoid steel it generally contains more cementite, hence a larger percent-

age of carbon. Moreover, while in true pearlite the carbon is probably wholly present as crystallized Fe_3C (cement carbon), in sorbite a part of it remains dissolved (hardening carbon), and it is probably to the presence of carbon in solution that sorbite owes its greater strength and its decreased ductility.

Showing the Properties of Pearlite and its Decomposition Product. Fe_3C represented Black.

Mechanical Properties of Mass.	Microstructure.	Segregation Stages.
Maximum tensile stress about 70 tons per square inch. Elongation on 2 inches = about 10 per cent.		1ST PHASE. "Sorbitic" pearlite with emulsified Fe_3C. Very dark on etching.
Maximum tensile stress about 55 tons per square inch. Elongation on 2 inches = about 15 per cent.		2ND PHASE. Normal pearlite with semi-segregated Fe_3C. Dark on etching.
Maximum tensile stress about 35 tons per square inch. Elongation on 2 inches = about 5 per cent.		3RD PHASE. Laminated pearlite with completely segregated Fe_3C. Exhibiting a play of gorgeous colours when lightly etched.
Maximum tensile stress about 30 tons per square inch.		4TH PHASE. Laminated pearlite passing into massive Fe_3C and ferrite.

NOTE.—It is important to remember that in a single section of steel two or even all three phases of pearlite may be observed in juxtaposition gradually merging into each other.

Fig. 189. — (Arnold.)

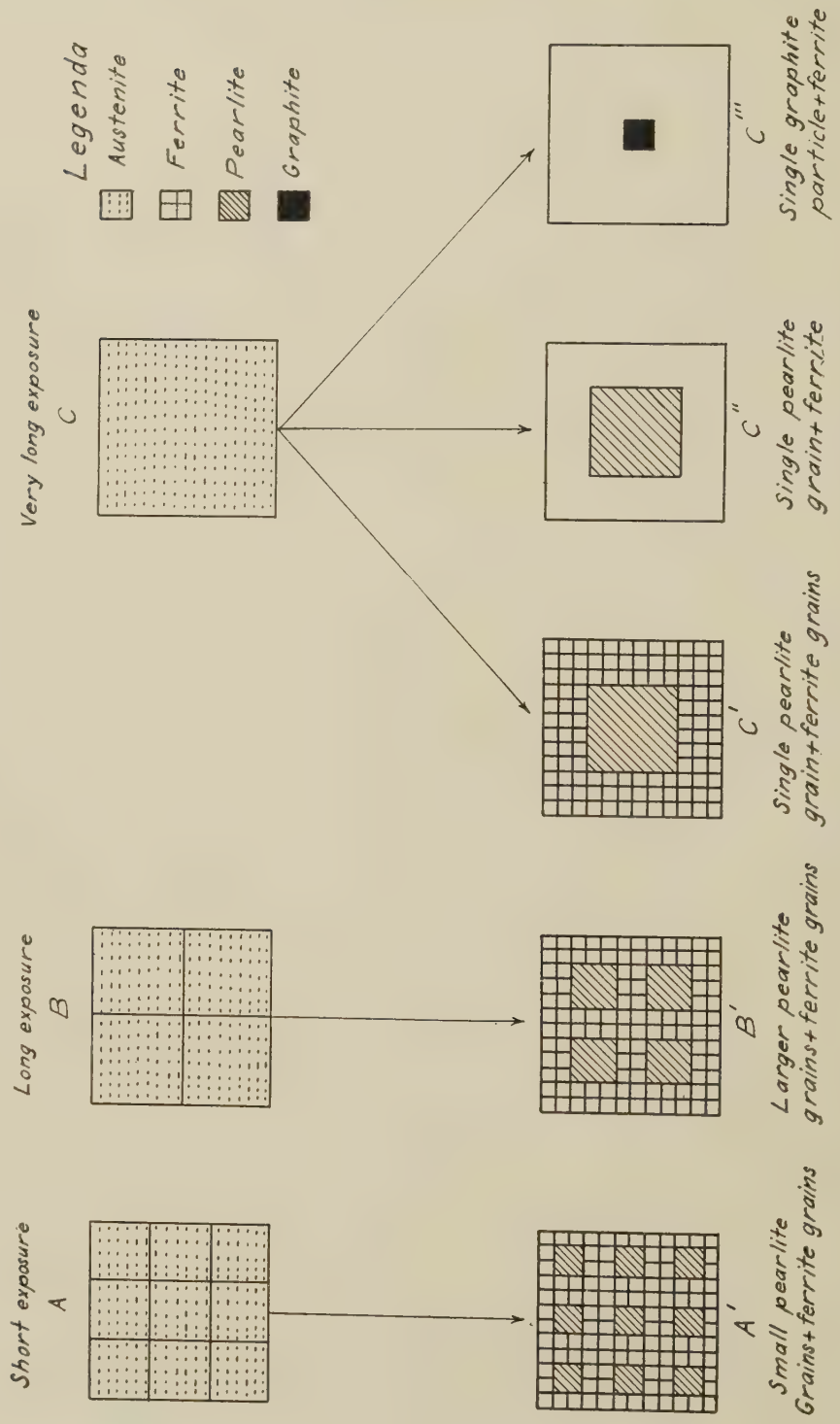

Austenite grains formed above Critical Range
Short exposure
A
Long exposure
B
Very long exposure
C
Legenda
Austenite
Ferrite
Pearlite
Graphite
A'
Small pearlite
Grains+ferrite grains
B'
Larger pearlite
grains+ferrite grains
C'
Single pearlite
grain+ferrite grains
C''
Single pearlite
grain+ferrite
C'''
Single graphite
particle+ferrite
Pearlite and ferrite grains formed on slow cooling though Critical Range

Fig. 190.

Crystalline Growth of Austenite Above the Critical Range. — Above its critical range steel is composed of polyhedral crystalline grains of austenite, which are made up of small crystals (probably octahedra) similarly oriented in the same grain but whose orientation changes from one grain to the next. Indeed it is this lack of uniformity of the orientation of the crystalline matter building up the grains that gives existence to these grains, for if all the small crystals of which they are composed were similarly oriented, clearly there would be but a single allotriomorphic crystal or grain. If steel be maintained for a long time above its critical range, the austenite grains of which it is composed show a tendency to grow in size through adjoining grains assuming like crystalline orientation and, therefore, merging into a single and correspondingly larger grain. This growth increases with the temperature and with the duration of the treatment. Given a sufficiently long time and sufficiently high temperature, but one grain must be formed. This, as already seen in Chapter X, is actually what takes place in meteorites during the cooling of which the prevailing conditions are such as to produce this uniformity of orientation. It follows from the above considerations that on annealing, if the metal be kept a long time above its critical range, even but slightly above it, a coarser austenite will be formed, which in turn implies, after slow cooling, a coarser pearlitic or sorbitic structure. In hypo-eutectoid steel the grains of austenite will expel some free ferrite, and in hyper-eutectoid steel some free cementite, before being converted into pearlite, but the final pearlite grains will nevertheless increase in size with the size of the original austenite grains. The structure of steel containing 0.50 per cent carbon kept two hours at 1150 deg. C. and cooled in air has been shown in Figure 171. The very large sorbitic grains formed prove the existence above the range of equally large, or even larger, austenitic grains. The cooling through the range was so rapid that but a small amount of free ferrite was separated, the sorbite grains, therefore, representing nearly the exact size of the austenite grains.

In Figure 190 an attempt has been made to depict this relation between the austenitic structure above the range and the corresponding pearlitic or sorbitic structure below the range. The steel considered is supposed to be hypo-eutectoid and to contain, after slow cooling, a large proportion of free ferrite. A is intended to represent a piece of this steel made up of nine relatively small austenitic grains formed on short exposure above the range. On cooling through the range ferrite is liberated and the residual austenite grains converted into as many pearlite grains as shown in A'. The small squares of the matrix surrounding the pearlite grains represent as many small ferrite grains. After a longer exposure, possibly at a higher temperature, the steel will be made up of larger austenite grains, say of four grains as shown in B, and these, on slow cooling through the range, will be converted after rejection of ferrite into four pearlite grains as indicated in B'. Theoretically, at least, we may assume that the temperature above the range may be so high and the exposure at that temperature so long that but a single austenite grain is formed, the entire mass having assumed a uniform crystalline orientation as shown in C. On slow cooling a single pearlite grain would then be formed surrounded by free ferrite in the form of small grains as depicted in C'. An exceedingly slow cooling through and below the range would have a tendency to cause the free ferrite to crystallize into larger grains and eventually to form but a single grain as indicated in C''.[1] Finally, as will be later

[1] Such slow cooling, as later explained, would also have a tendency to cause the spheroidizing of cementite.

explained, on very long exposure to a high temperature the cementite should, theoretically at least, be converted into as many graphite particles as there are austenite grains and, therefore, into a single graphite particle in case there is but a single grain of austenite, the steel then consisting, after slow cooling, of a kernel of graphite surrounded by uniformly oriented ferrite as shown in C'''. As already explained, however, this breaking up of cementite into graphite and ferrite does not take place unless a considerable amount of carbon is present, namely over 1 per cent.

The conditions depicted in A', B', C', C'', and C''' are conditions of equilibrium, according to the phase rule, since but two phases are present. It is now believed, however, that A', B', C', and C''' represent metastable equilibrium while C''', only, represents stable equilibrium. The phase rule will be considered in another chapter, when these remarks will be made clear.

CHAPTER XIV

THE HARDENING OF STEEL

References have already been made in these chapters to the invaluable property possessed by iron, containing a sufficient amount of carbon, of becoming extremely hard when rapidly cooled from a high temperature, as, for instance, by quenching in water from a bright red heat. This operation is known as the hardening of steel. The close relation existing between the hardening of steel and its critical range, which has also been alluded to, provides the key to the rationale of hardening. The operation consists of two distinct steps: (1) heating to the hardening temperature and (2) cooling from that temperature.

Heating for Hardening. — In order to harden steel it is necessary first to heat it above its critical range, because it is in passing through that range that it acquires hardening power. Any attempt at hardening it by cooling it suddenly from a temperature inferior to its critical range would result in but a very slight, if any, increase of hardness. It is evident, therefore, that to possess hardening power steel must be in the condition of a solid solution since the aggregate of ferrite and cementite formed on slow cooling through the critical range cannot be hardened by sudden cooling. The metal should not be heated much above the top of its range, because in so doing we coarsen its structure, as explained in previous chapters, while we do not increase, materially at least, its hardening power, and our aim in hardening should be to secure maximum hardness combined with finest possible structure. Quenching from a temperature greatly exceeding the critical range, moreover, increases the danger of warping and cracking the objects in the quenching bath. Nor should the steel be heated to a temperature much above its critical range and then cooled to that range before quenching, as sometimes recommended, because its structure is then likewise coarsened by the heating and slow cooling preceding the quenching. Clearly the rationale of the hardening operation consists in heating the metal just through its critical range, thus conferring to it both full hardening power and finest possible structure, and then in cooling it suddenly as soon as it emerges from its range, lest its structure be coarsened by heating above the range or by prolonged exposure at the quenching temperature. This judicious method of conducting the hardening operation is sometimes described as "hardening on a rising temperature." Let it be borne in mind that, since the position and width of the critical range vary in different steels, the most desirable quenching temperature will vary likewise. Low and medium high carbon steels should be quenched at higher temperatures than high carbon steel, for in order to acquire full hardening power they should be heated past their upper critical points, namely, Ac_3 or $Ac_{3\cdot2}$, as the case may be.

In practice, heating for hardening should be to some 20 to 50 deg. C. above Ac_1 in hardening eutectoid and hyper-eutectoid steels or above $Ac_{3\cdot2}$ in hardening hypo-eutectoid steel. The proper temperatures to which carbon steels should be heated

for hardening purposes and which are also those generally suitable for annealing the same steels have been shown graphically in Figure 163, Chapter XIII.

Some prefer to harden on a "falling temperature" by allowing the steel after it has emerged from its Ac range to cool until it is slightly above its Ar range before quenching. This permits quenching at a lower temperature, which in turn implies less danger of cracks occurring. It will not, however, generally yield so fine a grain.

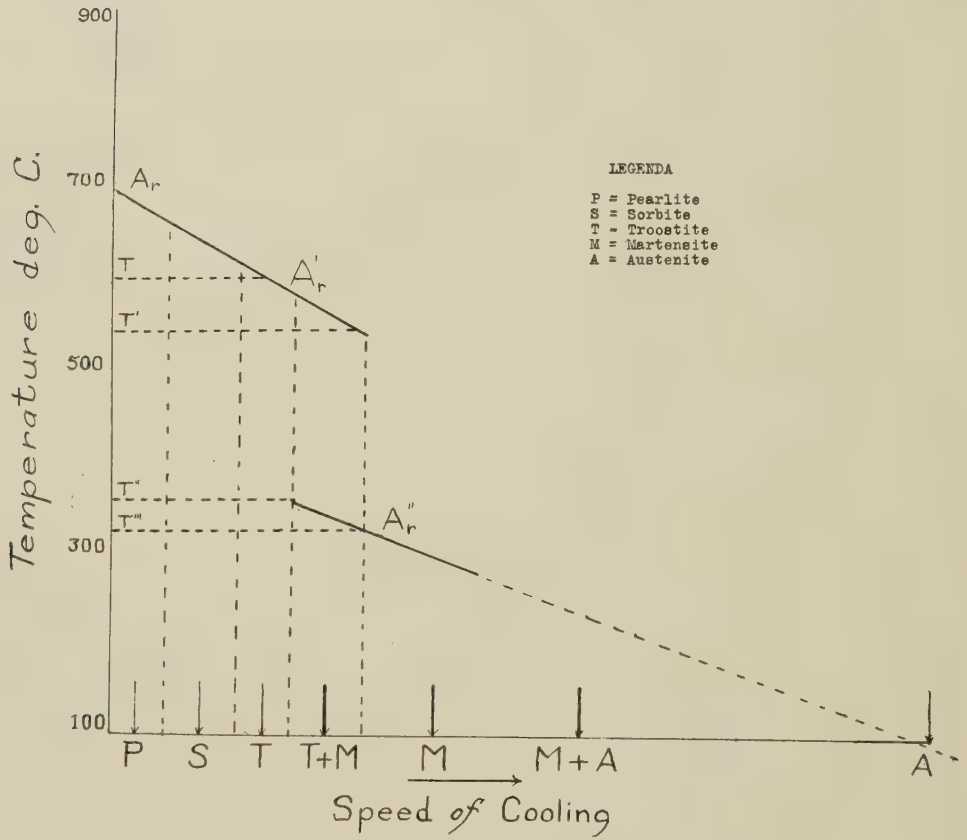


Fig. 191. — Speed of cooling vs. critical point and microstructure.

As explained in Chapter VII, increasing the temperature from which cooling begins results in a lowering of the critical point.

Heating for hardening should be slow enough to permit the steel to acquire gradually and evenly a uniform temperature throughout, and should not be too sudden, as for instance by placing cold steel in red-hot furnaces.

Generally speaking, large pieces should be heated to somewhat higher temperatures than small pieces for hardening purposes, it having been found (Benedicks and Mathews) that a higher temperature produces a quicker rate of cooling in the quenching bath. Mathews, for instance, states that a $\frac{3}{16}$-inch round bar of tool steel will harden at 750 deg. C., while a $\frac{3}{4}$-inch round bar of the same steel should be heated to 780 deg. C.

The use of lead or salt baths (chlorides and nitrates of sodium, calcium, potassium, and barium) for heating steel to the desired hardening temperature is to be

commended since it promotes uniformity of temperature throughout the pieces, while a suitably selected salt bath can readily be heated to, and maintained at, any desired temperature.

Time at Hardening Temperature. — Portevin thinks that the tensile strength of hypo- and of eutectoid steel increases with the duration of the heating before quenching, which he ascribes to the fact that the solution of the carbides is not instantaneous, time being required, especially in alloy steels. As noted elsewhere, a prolonged heating before cooling lowers the critical point.

Rate of Cooling vs. Position of Ar_1. — It is well known that increasing the speed of cooling from above the critical range results in lowering the point Ar_1. It is generally stated that in quenching, the point is lowered to so low a temperature that the transformation of austenite cannot proceed further than its first or martensitic stage, the steel being consequently hardened. It had been assumed that this lowering of the temperature at which the transformation takes place was gradual. Investigations conducted by French metallurgists, and more especially by Chevenard, by Portevin and Garvin, and by Dejean, have revealed the fact that this lowering of the transformation while at first gradual, becomes quite sudden for a certain cooling velocity called the "critical speed of quenching," or "critical cooling rate." These results have been confirmed by some American and other metallurgists and are now quite generally accepted. They constitute a notable progress in our understanding of the mechanism of quenching upon which the hardening of steel depends. Referring to Figure 191 (see also Chapter XII, Fig. 160), it will be seen that for a sufficiently slow rate of cooling the point Ar, and therefore the transformation which it implies, occurs at the normal temperature of 700 deg. C. ±. Austenite is here converted into pearlite. Whether such transformation implies, as was generally believed, gradual and successive formation of martensite, troostite, sorbite, and finally pearlite, or whether it consists of a direct transformation of austenite into pearlite, need not be considered for our present purpose, it being sufficient to note that pearlite is formed at that temperature.

On increasing the rate of cooling, the transformation point is gradually lowered, the steel assuming a sorbitic rather than a clearly pearlitic structure. Continued increase in the cooling velocity results in further depression of Ar to some 650 deg. C. accompanied by the formation of troostite. A *slightly* greater speed, and a second point occurs quite abruptly at a much lower temperature, corresponding to the formation of martensite. Finally the upper point disappears altogether, the lower one only persisting.

It will be noted that martensite forms when austenite transforms in the vicinity of 300 deg. C. The notations A′r and A″r have been proposed for these two points, which may be considered as a splitting up by rapid cooling of the Ar point. The speed of cooling required to cause the transformations to take place at 300 deg. C., and therefore the appearance of the A″r point, is called the critical speed of quenching. The intensity of the A′r transformation decreases as its temperature decreases from T to T′, while at the same time that of the A″r transformation increases as the temperature is lowered from T″ to T‴.

At the A′r point, according to Portevin and Garvin, troostite appears to form around the border of austenite grains, the central portions of the grains being subsequently transformed into martensite at the A″r point. Opinions differ in regard to the significance of the point A″r. Some believe it to be of a different nature from

the A′r transformation, while others regard it merely as the same transformation delayed by rapid cooling. The phenomenon of the double A′r-A″r transformation can be studied more effectively through the behavior of some alloy steels, because, as later explained, it now occurs on slow or relatively slow cooling, whereas in the case of carbon steels a very rapid cooling is required. Honda has observed that in steels containing 0.9 per cent carbon associated with 10 per cent nickel or 10 per cent chromium cooled in air the A′r transformation occurs at 700 deg. C. and the A″r at 450 deg. C. If the temperature is maintained for 18 minutes at 690 deg. C., that is after the A′r transformation has taken place, no A″r point can be detected and additional troostite instead of martensite will be formed. It is also noted, as should be expected, that the A″r point is lowered as the temperature from which cooling begins (T^{max}) is increased. It seems probable that after the A′r transformation has taken place, if the temperature is slightly lowered and then maintained, the A″r transformation completes itself the more slowly the lower that temperature. Honda calls the A′r-A″r transformation "stepped Ar_1 transformation."

Some writers appear to ignore the possible formation of sorbite in cooling through the critical range at the proper speed. Austenite, it would seem, according to them, transforms directly into pearlite on slow cooling at the normal critical temperature, directly into troostite when that temperature is lowered to some 600 deg. C., and to martensite when it is lowered to some 300 deg. C. Sorbite then could be formed only through the tempering (drawing) of martensite, as later explained. This contention is hardly acceptable, because we know that air cooling of small pieces results in a sorbitic structure. It may well be, however, that sorbite produced in this way does not possess the same properties as the sorbite resulting from the tempering of martensite, the latter being generally finer grained. Other significant differences may exist between them.

For like reasons we may well ask whether the troostite resulting from cooling through the range at the required speed is identical to the troostite resulting from the tempering of martensite. They are quite different in structure and may differ more deeply in properties than we at present suspect.

To sum up: (1) When the transformation takes place at the point Ar_1 (700 deg. C. ±), pearlite is formed; (2) when it takes place below 700 deg. C. but above temperature T (600 deg. C. ±), both sorbite and troostite are produced; (3) when it occurs partly between T and T′ and between T″ and T‴, both troostite and martensite are formed; (4) below T‴, martensite only; (5) were it possible to cause the transformation to occur considerably below 300 deg. C., the steel would probably remain partially untransformed and would contain both martensite and austenite, and (6) could the transformation be delayed to a temperature below room temperature, the steel would remain austenitic. It will be seen later that through the action of certain elements, such as manganese and nickel, it is possible to cause this lowering of the transformation below room temperature and to retain therefore the steel in its untransformed or austenitic condition.

The greater the speed of cooling required to attain the critical speed of quenching, that is to cause the transformations to occur at about 300 deg. C., the more superficial will be the hardening. It is why in carbon steel the hardened portion is relatively thin — not exceeding generally five to six mm., according to Portevin. Through the introduction of elements imparting self-hardening properties to steel, such as nickel and chromium, a much greater penetration of the hardening effect is obtained be-

cause the speed of quenching required to cause the transformations to occur at 300 deg. C. is very much less. Indeed, in air hardening steel, cooling in air suffices. When deep penetrations of the hardening effect is required, therefore, suitable alloy steels and not carbon steels should be used.

Rate of Cooling vs. Structure of Steel. — It has been made clear in the foregoing pages (1) that in order to retain much austenite in the cold the metal should be highly carburized and very quickly cooled from a high temperature; (2) that pearlite is produced by very slow cooling through the critical range, and (3) that in order to cause the formation of any of the three recognized transition constituents, namely

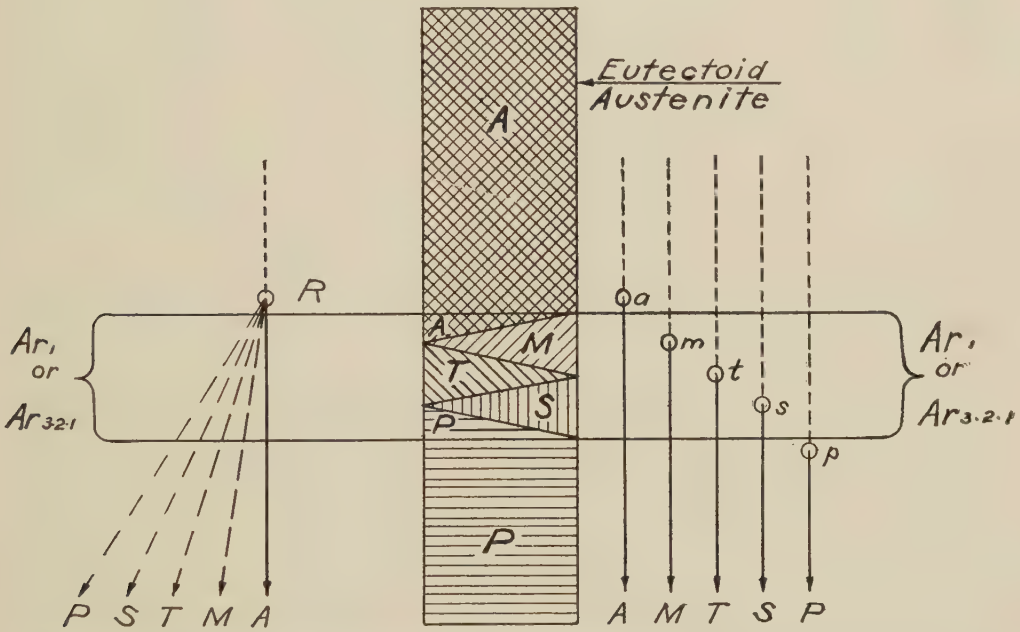


Fig. 192. — Diagram depicting the formation of austenite, martensite, troostite, sorbite, and pearlite in steel cooling through its critical range.

martensite, troostite, and sorbite, the steel should be cooled in such a way as to allow the formation of the desired constituent while preventing its further transformation, as, for instance, (*a*) by cooling the metal slowly to that portion of the range in which the constituent is formed, and then very quickly to atmospheric temperature, or (*b*) by cooling the metal at such a rate that austenite will transform at a temperature high enough to permit the desired constituent to form, to wit, cooling in water for martensite, in oil for troostite, in air for sorbite, but too low to permit its further transformation.

An attempt has been made in Figure 192 to give a graphical illustration of the cooling conditions needed for the production of the various constituents of steel. Its interpretation will be obvious. The critical range, or rather the lower critical point, Ar_1 or $Ar_{3\text{-}2\text{-}1}$, is represented as covering a considerable range of temperature so as to afford the necessary room for the diagrammatical representation of the formation, within that range, of the transition constituents. The diagram indicates that as the metal cools slowly through its range it does not pass abruptly from an

austenitic to a martensitic condition, and then to troostite, etc., but that these transformations are, on the contrary, gradual, the following types of structure being formed, theoretically at least: austenite, austenite plus martensite, martensite, martensite plus troostite, troostite, troostite plus sorbite, sorbite, sorbite plus pearlite, and pearlite. The transformations depicted refer to eutectoid steel or to the residual austenite (necessarily of eutectoid composition) of hypo-and hyper-eutectoid steel formed on slow cooling to Ar_1 after rejection of free ferrite or free cementite. In the case of these steels, therefore, free ferrite or free cementite is present in the above structures unless, indeed, cooling between Ar_3 and Ar_1, or between Ar_{cm} and Ar_1 has been so rapid as to prevent their separation. While, theoretically, very quick cooling from *a* to atmospheric temperature should retain the steel in its austenitic condition, even under the most favorable conditions, this can be done but partially, considerable martensite being produced. Cooling slowly to *m* and then quickly should produce martensite, while slow cooling to *t* or *s* followed by quick cooling should produce, respectively, troostite and sorbite. Slow cooling to *p*, followed or not by quick cooling, results in the formation of pearlite. Slow cooling to intermediate points between *m* and *t* or *t* and *s*, etc., should, theoretically, cause the formation of martensite and troostite, troostite and sorbite, etc.

These conditions may be realized in the same piece of steel by heating one end of a steel bar, preferably of eutectoid or hyper-eutectoid composition, well above the critical range and quenching the whole bar in ice-cold water. It is evident that, since at the time of quenching the temperature of the bar decreased gradually from the hot to the cold end, a portion of the bar must have been quenched while in the martensitic condition, another while in the troostitic condition, etc. The preparation and microscopical examination of longitudinal sections through the center of the bar should reveal the existence of the various constituents indicating as many stages in the transformation of austenite.

On the left of the diagram, five lines starting from the point *R* above the critical range represent coolings through the range at different speeds, as, for instance, (1) very quickly in ice-cold water, (2) quickly in water, (3) less quickly in oil, (4) slowly in air, and (5) very slowly in furnace, resulting, respectively, in the formation of austenite (or rather austenite and martensite), martensite, troostite, sorbite, and pearlite, or, more frequently, of mixtures of two or even three of these constituents.

These conditions may be realized in the same piece of metal by heating a steel bar of considerable cross section (not less than 1 inch in diameter) and preferably of eutectoid or hyper-eutectoid composition to a temperature well above the critical range and quenching it in water. The cooling should be rapid enough to cause the formation of martensite near the outside of the piece while the cooling of the center should be so slow (because of the size of the bar) as to permit the formation of pearlite. Between the martensitic shell and the pearlitic core the metal should be composed of the other transition constituents, that is, starting from the center, of sorbite and then of troostite. The microscopical examination of a cross section through the bar should reveal this gradual change of structure from center to outside.

The formation of a transition constituent through the tempering of a constituent representing a less advanced, and therefore less stable, stage of transformation has already been alluded to and will be considered at greater length in the next chapter. It has already been mentioned that, according to some, austenite transforms directly

into pearlite at a high temperature, and to troostite at a lower temperature, without first passing through the martensitic stage. These views do not appear to be well supported.

It has been seen that to harden steel, the metal should be heated above its Ac range in order to acquire hardening power, that it should be heated but slightly above that range in order to acquire a fine grain, and that it should be cooled rapidly enough before reaching the Ar range to cause the transformation of austenite to occur at some 300 deg. C. or lower, generally by immersing it in a medium capable of rapidly abstracting heat from it. The increase of hardness will be the greater the higher the carbon content, at least up to the eutectoid point, and the more rapid the cooling; the latter, in turn, depending upon the size of the object hardened and the nature of the quenching bath, i.e. its power of abstracting heat from the cooling mass. It was long thought that this so to speak cooling power of the bath depended chiefly, if not solely, upon its temperature at the time of immersion and upon its heat conductivity. It was believed, for instance, that mercury was a more effective cooling medium than water because of its greater conductivity for heat, that cold water was more effective than tepid water because of its lower temperature, etc. Recent investigations appear to show, however, that the cooling power of a quenching bath is, within limits, quite independent of its actual temperature and of its heat conductivity, and even of its specific heat. Benedicks contends that it depends almost exclusively upon its latent heat of volatilization. Its temperature, however, should be low enough to prevent the adherence of vapor bubbles to the metal. In accordance with these views mercury, in Benedicks' opinion, is inferior to water, while saline solutions are not superior to it. Methyl alcohol, on the contrary, is a more effective cooling medium for hardening than water. According to Le Chatelier, also, mercury is less effective than water, but in his opinion because of its lower specific heat. Le Chatelier believes that the specific heat of the liquid is the most important factor influencing its value as a cooling medium, its conductivity being of secondary importance, the loss of heat taking place more through circulation than through conductivity. On the other hand, Benedicks contends that the rate of flow has very little influence.

According to Mathews (1) the rate of cooling in water quenching remains quite constant up to a water temperature of 37 deg. C.; (2) brine solutions not only produce a quicker rate of cooling but retain their cooling power practically unimpaired so long as their temperature remains below 65 deg. C.; (3) while oil baths produce a slower rate of cooling, they can be heated to considerably higher temperatures than water or brine before having their cooling power seriously diminished.

Portevin and Garvin list under "Laws of Cooling" the following factors as influencing the speed with which any quenched steel cools:

(1) Temperature at the commencement of quenching, or actual quenching temperature; (2) mass, form, and dimensions of sample; (3) position of a given point in the interior of the sample; (4) nature of the bath — that is to say, of the medium in which quenching takes place — which acts according to its physical properties, particularly its specific heat, its latent heat of vaporization, its conductivity, and its viscosity; (5) the temperature of the bath, which may vary during the process of cooling, according to the respective masses of the bath and of the sample; (6) agitation of the bath in relation to the sample; (7) state of the surface of the sample; (8) temperature at the end of the cooling.

Contraction of Hardened Carbon Steels. — It has been observed that hardened carbon steels contract for a long time after they have been hardened and that such contraction is accompanied by some evolution of heat. Contractions lasting several months have been reported. Sir Robert Hadfield and Brush attribute this contraction to the fact that after quenching, steel is in a highly strained condition, and that the gradual relief of strain following the quenching results in a spontaneous evolution of heat accompanied by contraction until a condition stable at room temperature is reached.

The phenomenon has been further investigated by Tokujirô Matsushita, who offers the following conclusions:

(1) In the case of steels which are imperfectly hardened, there is always a gradual elongation, or an elongation associated with a subsequent contraction. (2) In steels which are well hardened, there is always a gradual contraction. (3) The elongation is explained by the incomplete Ar_1 transformation, while the contraction is due to separation of unstable cementite from its solid solution, — the martensite. (4) The complete separation of the first unstable cementite at room temperature requires several months or over one year; but by heating the steel to about 100 deg. C. the same separation follows within two hours. (5) The separation of the unstable cementite does not affect the hardness of the steel appreciably, but the separation of the more stable cementite is associated with a loss of hardness. (6) The electric resistance of a steel considerably increases by quenching, and decreases by tempering; this increase is due to the cementite in solid solution. (7) The gradual elongation or contraction of quenched steel is always accompanied by an evolution of heat. This heat is the heat of transformation, but is not caused by yielding strain, as was generally supposed to be the case.

Quenching Cracks. — Those who are engaged in the commercial hardening of steel are ever concerned lest the hot metal suddenly immersed in a cold medium develop cracks which may entirely ruin the quenched article. They are ever anxious to learn their causes and to prevent, if possible, their occurrence.

The best way to instruct is to quote those who speak with authority. Portevin states that quenching cracks occur generally (1) at the end of the quenching, and (2) in the first period of tempering if it be done carelessly, this in his opinion being the chief source of quenching cracks. To minimize the danger of quenching cracks Portevin gives the following advice:

(1) Rejection of pieces presenting physical defects before quenching; (2) preliminary annealing or prolongation of heating before quenching; (3) uniform heating; (4) quenching at lowest possible temperature; (6) quenching as slowly as possible compatible with the hardness and other properties desired; (7) uniform cooling; (8) elimination of sharp angles and great inequalities in the pieces to be quenched; (9) tempering to follow immediately the quenching treatment.

In a general way, water quenching is to be preferred to oil quenching if it can be performed without producing quenching cracks, and the purer and sounder the steel, the freer from segregation and inclusions, the less the danger of these cracks occurring.

Unger writes that it is "practically impossible to water-quench a 10-inch hollow axle containing one per cent carbon without breaking it in several pieces" and that there is great danger of cracking large forgings in water quenching.

Portevin states that sand blasting after immersion in kerosene is useful in detecting quenching cracks.

Steel of Maximum Hardening Power. — From the above considerations it will be obvious that the hardening of steel consists in preventing the formation of relatively soft pearlite and in causing, instead, the formation and retention of hard martensite or troostite or, more often, of both. It follows from this that the steel possessing maximum hardening power must be that steel which in slow cooling would contain most pearlite, namely, eutectoid steel. It does not, of course, mean that quenched eutectoid steel is harder than quenched hyper-eutectoid steel, but merely that the *increased hardness* produced by quenching is greatest in the case of eutectoid steel. Quenched hyper-eutectoid steel is harder than quenched eutectoid steel because of

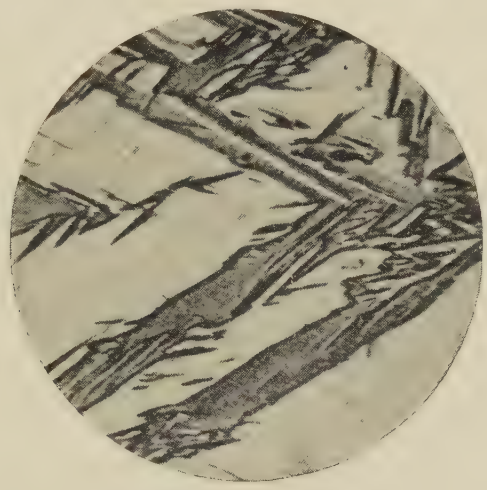


Fig. 193. — Steel. Carbon 1.57 per cent. Magnified 1000 diameters. Heated to 1050 deg. C. and quenched in ice water. (Osmond.)

the presence in the former of some free cementite or of more highly carburized martensite, but the difference of hardness between the two steels is greater before quenching.

Hardening Large Pieces. — In hardening pieces of considerable cross section it is evident that the central portions will not cool so quickly as the outside and will not, therefore, be so hard. Indeed the center may cool so slowly that it will fail to harden at all. The limitation of the hardening process, as applied to large pieces, will, therefore, be evident. It is seldom desirable, however, to harden large pieces to their very core. When large steel objects are to be hardened, as for instance in the case of armor plates, superficial hardness only is generally desired, or at least hardness penetrating to but a relatively small depth, and this is readily secured through the case-hardening process.

The influence of mass in cooling for hardening is well illustrated by Le Chatelier, who states that a steel bar containing 1.00 per cent carbon and measuring 10 mm. in diameter when quenched in water is wholly martensitic, whereas the same steel in the form of bars 50 mm. in diameter is entirely troostitic after quenching, intermediate sizes being mixtures of martensite and troostite.

When it is imperative to harden to the core, alloy steels of the variety known as self or air hardening should be used (see Chapter XIX).

AUSTENITE

Nature of Austenite.[1] — Austenite is universally considered as a solid solution of carbon, or of the carbide Fe_3C in gamma iron.[2] All steels above their critical range are made up of this solid solution. It follows that the carbon content of austenite varies, like that of steel, from a mere trace to some 1.75 per cent. It is not, therefore, a constituent of constant composition.

Occurrence of Austenite. — While present in all steels above their critical range, much austenite is very rarely found in ordinary steels at room temperature even on

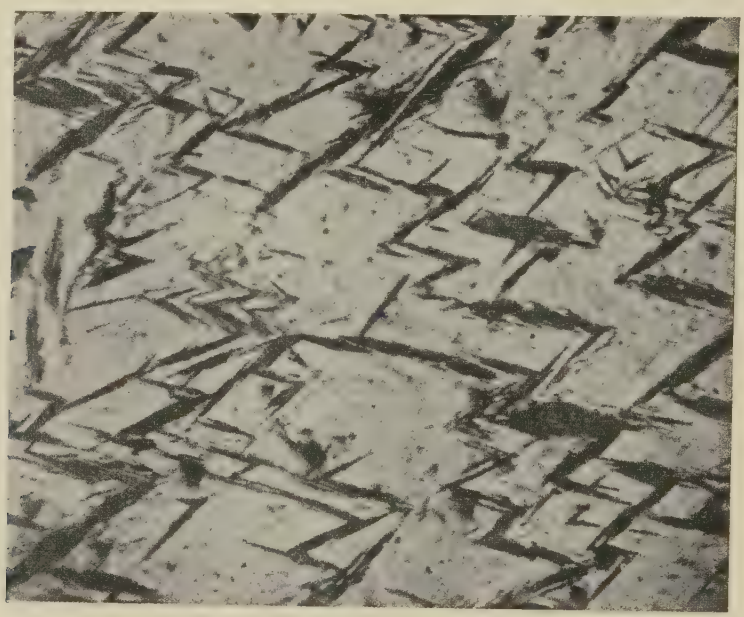


Fig. 194. — Steel. Carbon 1.57 per cent. Magnification not stated. Heated to 1050 deg. C. and quenched in ice water. (Osmond.)

fast cooling. This is due to the rapidity with which austenite is transformed on cooling through the critical range if not into an aggregate of ferrite and cementite, at least into some transition stages, namely sorbite, troostite, or martensite. In the commercial hardening of ordinary carbon steel the passage of the metal through its range is never sufficiently rapid to retain in the cold more than a small amount of undecomposed austenite. To prevent the transformation of austenite the conditions generally affecting the hardening of the metal must be, so to speak, greatly intensified: (1) The steel should be highly carburized, (2) quenching should be from a high temperature (1000 deg. C. or more), and (3) a very effective quenching bath should be used, such as ice-cold water or brine. In Figures 193 and 194 are shown, after Osmond, the structure of steel containing 1.57 per cent carbon heated to 1050 deg. C. and quenched in ice water. The magnification is 1000 diameters. The dark-colored, zigzag constituent is martensite; the light matrix, or background, is austenite. By

[1] This name was suggested by Osmond in honor of the late Sir William Roberts-Austen. Austenite has also been called mixed crystals and gamma iron and by some writers, wrongly, martensite.

[2] Arnold believes that austenite is the carbide $Fe_{24}C$ (hardenite) holding in solution ferrite in hypo-eutectoid steel and cementite in hyper-eutectoid steel.

the drastic quenching treatment just described it is possible, in the case of high carbon steel, to retain more than one half of the steel in its austenitic condition. A similar structure by Lucas, magnified 2100 diameters, is shown in Figure 195. A broad twin will be noticed in the austenite.

The retention of austenite in the cold is greatly helped by the presence of some elements, such as manganese and nickel, which lower the position of the transforma-

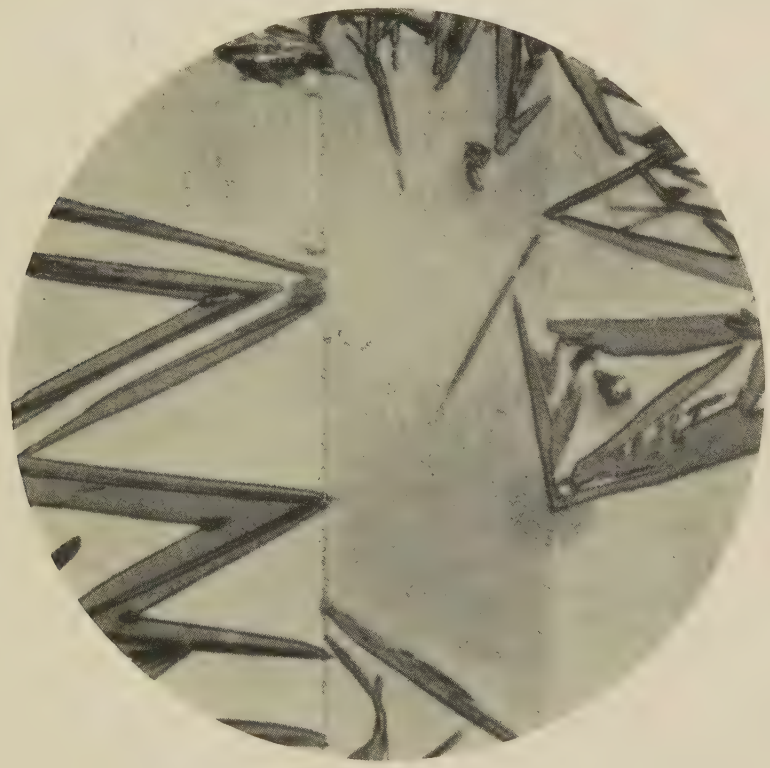


Fig. 195. — Austenite and martensite. Magnified 2100 diameters. (F. F. Lucas.)

tion range, eventually depressing it below atmospheric temperature and, therefore, causing the steel to remain austenitic even after slow cooling. As the manganese increases the retention of austenite becomes easier, that is the quenching need not be so drastic nor the carbon content so high. Finally with 10 or more per cent of manganese and 1 or more per cent carbon, or with 25 per cent nickel, the steel remains austenitic after slow cooling. The structure and properties of austenitic steels will be considered in another chapter.

To sum up: (1) Some austenite may be retained in the commercial hardening of ordinary carbon steel; (2) more of it may be retained in the cold, associated with considerable martensite in quenching very high carbon steel, from a very high temperature in ice-cold water, as, for instance, by quenching steel containing not less than 1.50 per cent carbon from 1000 deg. C. or higher; (3) in the presence of 1 per cent of manganese very small pieces of very high carbon steel may be retained wholly in their austenitic condition by quenching them from a very high temperature, as,

for instance, by quenching in ice-cold water from 1400 deg. C. small pieces of steel containing 1 per cent of manganese and not less than 1.5 per cent carbon (Robin); (4) with increasing proportions of manganese the transformation of austenite may be prevented in steel containing less carbon and quenched from lower temperatures (Maurer); (5) manganese steels containing, for instance, 10 or more per cent manganese and 1 or more per cent carbon remain austenitic after slow cooling; (6) nickel steel containing some 25 per cent of nickel likewise remains austenitic on slow cooling.

It will be seen in Chapter XIX that other elements besides manganese and nickel may, in the presence of a sufficient percentage of carbon, cause the steel to remain untransformed, that is, austenitic even after slow cooling.

Benedicks contends that in the preservation of austenite in carbon steel by rapid cooling an important part is played by the very great pressure to which the metal is subjected, (1) because of the shrinkage of the exterior portion or outer shell on the interior and (2) because of the dilatation accompanying the change from gamma to beta or alpha iron. Were it not for this pressure Benedicks believes that the transformation of austenite could not be prevented. As an evidence of this he shows that austenitic steels produced by quenching are austenitic only in their interior, i.e. where the pressure had been greatest, the outside layers in which the pressure was small or nil being martensitic. He shows further, that on removing by grinding the martensitic shell, the austenitic core in turn becomes martensitic, owing to the removal of the pressure exerted upon it by that shell. Again the quenching of steel cylinders surrounded by cast-iron shells resulted in the formation of austenite close to the skin of the steel cylinders, owing apparently to the very great pressure exerted upon the steel by the contraction of the iron shells.

Dr. Mathews has reported the frequent occurrence, especially in steels capable of hardening readily in oil, of a larger proportion of austenite in oil-quenched samples than in water-quenched samples. This is contrary to what should be expected, in accordance with our conception of the nature of austenite and of its transformation.

Mathews writes: ". . . why does oil hardening retain more gamma iron than water hardening in a considerable variety of steels? It is believed that a more intensive investigation of quenching stresses rather than of quenching rates may afford an explanation. May it not be that this is an important function of the commoner alloys, chromium and manganese, and their mixtures with nickel, vanadium, molybdenum, and others, to promote the retention of austenite, and that to this fact is due some of the properties of alloy steels as compared with carbon steels?"

Dr. E. C. Bain believes that "the more violent quenching stresses actually deform the austenite grains and cause transformations." He also believes that the stronger atomic bonding between unlike atoms, which is necessary for any solid solution, is the cause for the easier retention of austenite in alloy steels.

It has been observed that on tempering hardened (martensitic) steel a contraction first occurs, resulting from the transformation of martensite, this being followed, at a higher temperature, by an expansion resulting from the transformation of austenite into martensite (or troostite) with augmentation of volume.

Dr. Mathews writes: "It is known that hardened steel is lighter than annealed steel; in fact, martensite is the lightest, that is, the most voluminous condition of steel. A hardening which produces the lowest specific gravity (greatest volume) may be considered as the most complete martenisation possible for that steel. A hardened steel of greater specific gravity (smaller volume) must indicate retained austenite,

or that the hardening has gone beyond the martensite stage toward troostite or pearlite."

Etching of Austenite. — The etching reagents usually applied to bring out the structure of unhardened steel, namely, picric acid and nitric acid, do not always yield satisfactory results in the case of hardened steel. Kourbatoff discovered a complex reagent which often produces greater contrast between the various constituents. It is made up by mixing one part of amyl alcohol, one part of ethyl alcohol, one part of methyl alcohol, and one part of a 4 per cent solution of nitric acid in acetic anhydride and should be prepared just before use.

Heyn recommends for etching hardened steel a solution containing one part of hydrochloric acid and 99 parts of absolute alcohol. More uniform results are obtained if a weak current of electricity be passed through the solution, the samples to be etched forming the positive pole while the negative electrode may consist conveniently of a piece of sheet lead. With the assistance of the electric current the use of a very dilute aqueous solution is advisable, namely, one part of hydrochloric acid in 500 parts of distilled water.

Osmond, likewise, used successfully a solution of 10 per cent of hydrochloric acid in water by which the martensite is colored darker than austenite, the treatment requiring several minutes. Osmond writes: "There is more regularity obtained by having the specimen connected, by means of a platinum wire, with the positive pole of a bichromate cell, a strip of platinum placed in the acid being connected with the negative pole. In this way the specimen becomes the anode, and the platinum the cathode."

Benedicks recommends for the etching of martensito-austenitic steel a 5 per cent alcoholic solution of metanitrobenzol-sulphonic acid, which always darkens martensite more than austenite. Immersions of some fifteen seconds are generally sufficient.

Structure of Austenite. — When austenite and martensite occur in the same sample the latter is generally colored darker (Figs. 193 to 195). Martensite, moreover, is readily distinguishable because of its zigzag or needle shape. Some writers claim that martensite is sometimes colored less than austenite. Indeed Maurer contends that this is always so, arguing that if most photomicrographs indicate the contrary it is because the martensite had undergone a certain amount of tempering resulting in the formation of some troostite, as later explained. According to this writer, in order to prevent any tempering of the martensite, and therefore the formation of dark-colored troostite, great care must be exercised in sawing, polishing, etc. To this Benedicks replies that it cannot always be so, for in quenching austenite in liquid air martensite is formed, which must be free from troostite and which, nevertheless, is darker than austenite. It may be asked, however, whether it is certain that the martensite produced in this way is actually free from troostite. Evidences of a more conclusive nature are needed to account satisfactorily for the shifting in the relative coloration of austenite and martensite when occurring side by side. Pure austenite is made up of polyhedral grains[1] (see Chapter XX for the structure of austenitic steels), which, as explained in previous chapters in connection with the structure of gamma iron, are undoubtedly made up of true crystals — small octahedra according to Osmond. It should be noted that when austenite occurs in the presence of much

[1] Because of this structure Guillet and some other writers refer to steels composed of austenite as "polyhedral" steels. This does not seem advisable as it may lead to confusion, for other steels also have polyhedral structures, to wit, very low carbon (ferritic) steels.

martensite (Fig. 193) its polyhedral structure is not brought out. Twinnings are frequently observed in austenite (see Chapter III, Fig. 34), although it has been claimed that they form only after straining, especially if followed by annealing.

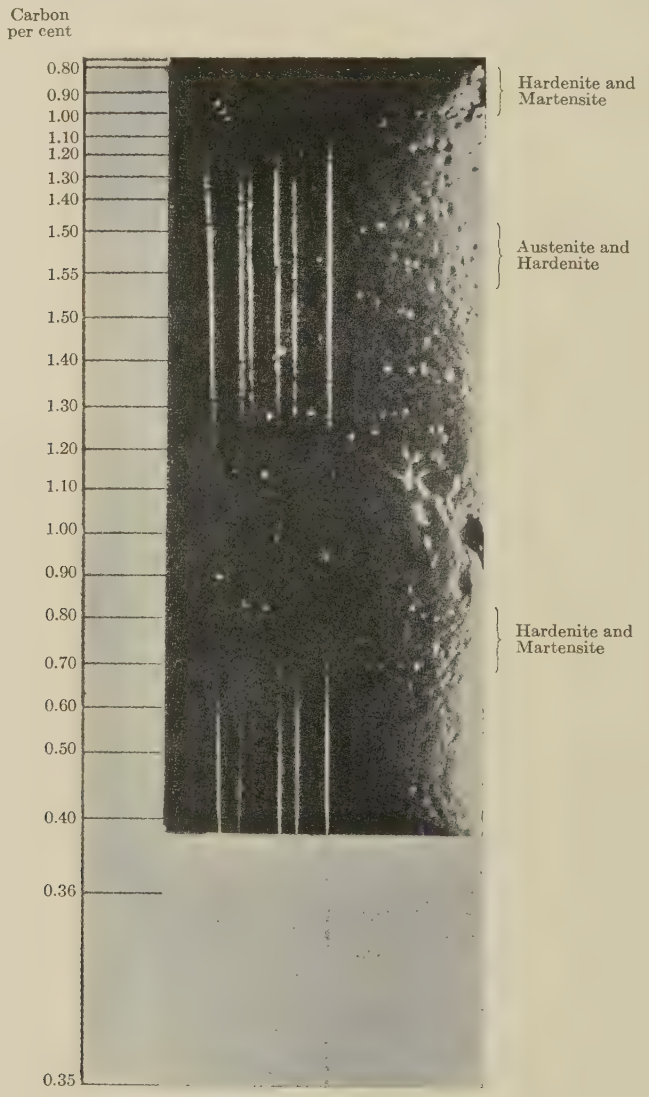


Fig. 196. — Showing the relative softness of austenite. (Osmond.)

Baykoff succeeded in etching austenite above the critical range of the steel, that is in a range of temperature where it is stable. He accomplished this by heating polished steel samples in a porcelain tube through which a current of hydrogen was kept circulating and by passing through it gaseous hydrochloric acid when the desired temperature had been obtained. The resulting structures were found to be polyhedral even in the presence of very little carbon, thus confirming the previous belief as to the crystalline character of austenite.

The author has found that the action of hydrogen gas is sufficient to bring out the structure of austenite at a high temperature, the use of hydrochloric acid being unnecessary (see Chapter III, Fig. 34).

Properties of Austenite. — Since the carbon content of austenite varies from a mere trace to 1.70 per cent it may well be expected that its physical properties will likewise vary, i.e. that it will increase in hardness and strength and decrease in ductility as the carbon increases. Osmond was the first to show conclusively that austenite is softer than martensite of identical carbon content. Figure 196 represents the structure of a bar of steel containing 1.55 per cent carbon in the center and a gradually decreasing amount towards the outside. This bar was heated to 1050 deg. C. and

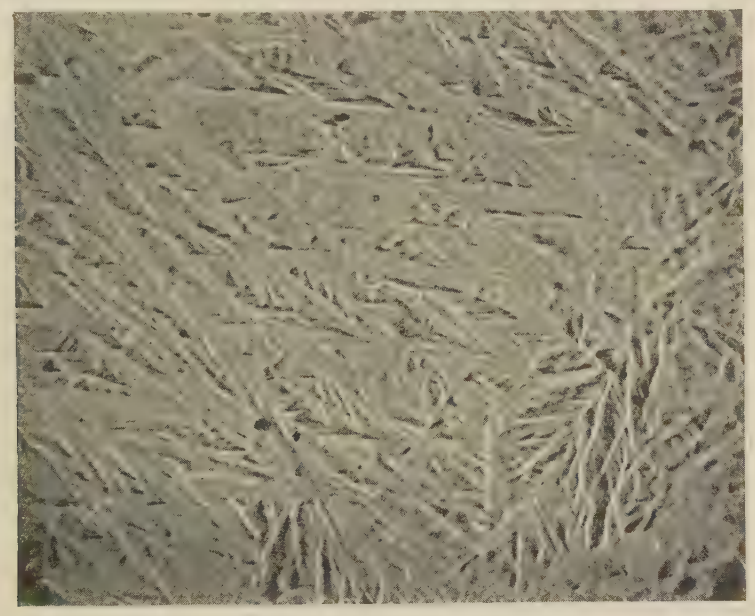


Fig. 197. — Nickel austenitic steel quenched in liquid air. Magnified 250 diameters. (Osmond.)

quenched in mercury at a temperature of −9 deg. C. After polishing but before etching, a needle was repeatedly drawn across it from end to end with even pressure. The photograph clearly shows that the needle scratched the steel (1) where it contains so little carbon (0.40 to 0.60 per cent) that it was only partly martensitic and hence relatively soft, (2) in those regions which because of very high carbon content (1.30 to 1.55 per cent) were partly austenitic, and (3) that it failed to scratch it in those regions which because of a more moderate amount of carbon (0.70 to 1.20 per cent) were fully martensitic and therefore very hard. It is also well known that high carbon austenitic manganese steel, while extremely difficult to machine, can be readily scratched by a needle, being mineralogically much softer than high carbon martensitic steel.

Since steel above its critical range is non-magnetic, we should expect steels which remain austenitic in the cold to be non-magnetic. This we know to be the case, for manganese as well as nickel austenitic steels are non-magnetic.

Some of the physical properties of austenite may be inferred from the known

properties of austenitic steels such as manganese and high nickel steels. These are known to be very ductile (after suitable heat treatment), tenacious, of low elastic limit, to possess very high resistance to wear, although their mineralogical hardness is not excessive, and to be machined only with great difficulty. They have, like gamma iron, a very high electrical resistance.

It has already been pointed out that the crystallization of austenite is probably cubic, the octahedron being its prevailing crystalline form. Le Chatelier, however, believes that austenite crystallizes in the orthorhombic system with octahedral cleavage.

On slow cooling through the critical range in the absence of considerable quantities of retarding elements such as manganese and nickel, austenite rejects a sufficient

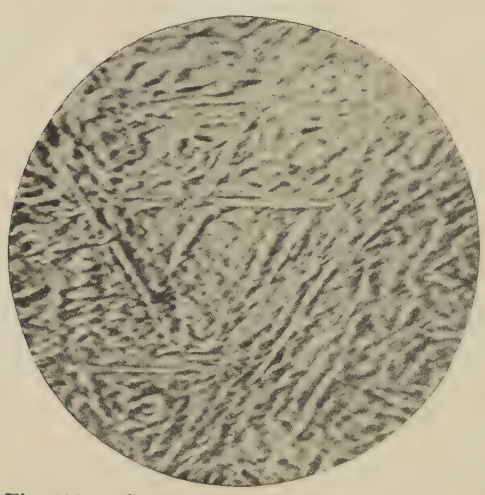


Fig. 198. — Steel. Carbon 0.45 per cent. Magnified 1000 diameters. Heated to 825 deg. C. and quenched at 720 deg. (Osmond.)

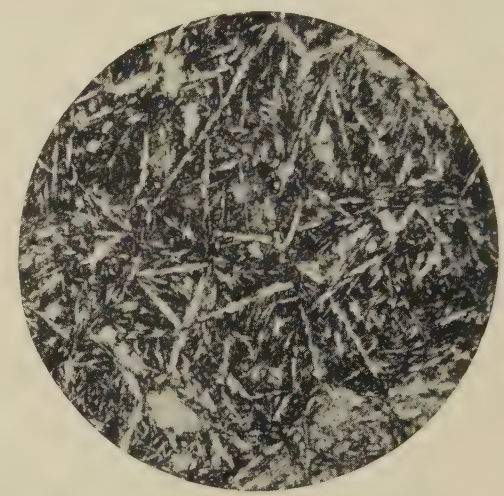


Fig. 199. — Steel. Carbon 1.25 per cent. Magnified 150 diameters. Heated to 1232 deg. C. and quenched in oil. (C. C. Buck, Correspondence Course student.)

amount of ferrite in hypo-eutectoid, or of cementite in hyper-eutectoid, steel to assume the eutectoid composition (0.85 per cent C. or thereabout) when it is converted bodily into pearlite. This transformation is probably not sudden, however, several transition constituents being formed, namely, martensite, troostite, and sorbite.

It will be seen in another chapter that on tempering austenite, that is on reheating it below the critical range of the metal, it is likewise converted gradually and successively into martensite, troostite, and sorbite, or according to some writers directly into troostite and then into sorbite.

Quenching nickel austenitic steel in liquid air results in the formation of martensite with increased volume, causing swellings of the polished surface as shown in Figure 197.

MARTENSITE

Nature of Martensite.[1] — It is generally believed (1) that martensite corresponds to an early stage of the transformation of austenite in passing through the critical

[1] This name was selected by Osmond in honor of A. Martens, a distinguished German metallurgist and testing engineer.

range, or (2) that it is formed only when austenite transforms in the vicinity of 300 deg. C. because of rapid cooling, or of the presence of so-called "retarding" elements. The nature and formation of martensite will be discussed at greater length in Chapter XVI, under "Theories of Hardening." Arnold believes that martensite is, like austenite, the carbide $Fe_{24}C$ holding in solution ferrite in hypo-eutectoid steel and cementite in hyper-eutectoid steel.

Occurrence of Martensite. — Martensite is most readily obtained by quenching small pieces of high carbon steel in cold water; in the case of large pieces, while the

Fig. 200. — Structure of martensite. Magnified 3230 diameters. (F. F. Lucas.)

outside portion may be martensitic their center is likely to be partly troostitic. In low carbon steel it is more difficult still to prevent the formation of some troostite, while in steel containing very little carbon, free ferrite as well is likely to be present. In high carbon steel some free cementite is generally associated with the martensite as well as undecomposed austenite.

Etching of Martensite. — Dilute alcoholic solutions of picric, nitric, or hydrochloric acid generally bring out satisfactorily the structure of martensite, but the Kourbatoff reagent, already described, sometimes yields better results. Martensite generally darkens more quickly than austenite but always remains much lighter than troostite.

Structure of Martensite. — Martensitic structures are shown in Figures 198 and 199, and under very high magnification, after Lucas, in Figure 200. The white

constituent in his illustration indicates the presence of untransformed austenite and the very dark one of troostite resulting from the transformation of martensite. Osmond describes the structure of martensite as consisting of three systems of fibers, respectively parallel to the three sides of a triangle and crossing each other frequently. Osmond also states that when the metal contains less carbon the needles are longer and more clearly differentiated, other things being equal. According to crystallographers these markings, in reality cleavages of octahedra, indicate crystallites of the cubic system and, therefore, afford an additional evidence of the cubic crystallization of austenite from which martensite is derived. Osmond and Cartaud refer to them as probable pseudomorphs of twinnings due to tension, occurring in gamma iron through partial formation of the bulky beta and alpha modifications.

Properties of Martensite. — The carbon content of martensite varies from a mere trace to as much as 1 per cent, and possibly more, in very suddenly cooled hypereutectoid steels. In high carbon steels, however, it is difficult to prevent the setting free of much of the excess cementite even on very quick cooling. From this variation of its percentage of carbon it follows that the properties of martensite must also vary. As the carbon increases its hardness and strength increase while its ductility decreases, martensitic steels being generally hard and brittle, and therefore unforgeable in the cold.

It will be seen in another chapter that on heating martensite below the critical range, i.e. on tempering it, it is converted first into troostite and then into sorbite.

TROOSTITE[1]

Nature of Troostite. — Troostite is generally believed to be an extremely fine aggregate of the carbide Fe_3C and alpha iron, compared by some to a colloidal solution.[2] Clearly, then, it would seem to be martensite in the process of being transformed into sorbite and pearlite.

In the report of the Committee on the Nomenclature of the Microscopical Constituents of Iron and Steel of the International Association for Testing Materials, troostite is defined as follows: "probably aggregate. In the transformation of austenite, the stage following martensite and preceding sorbite . . . An uncoagulated conglomerate of the transition stages."

The nature and formation of troostite is further considered in Chapter XVI.

Occurrence of Troostite. — In order to produce troostite on cooling steel from above its critical range, it is necessary that the cooling through the range should be so regulated as to allow it to form and at the same time prevent its further transformation (into sorbite and pearlite). These conditions may prevail (1) in cooling slowly to the middle of the range, thus permitting the formation of troostite (see Fig. 192), and then very quickly to atmospheric temperature, thus retaining troostite, or (2) in cooling at such rate that the Ar_1 point is depressed to some 600 to 650 deg. C., as, for instance, quenching large pieces in water when the central portions at least will be troostitic, or quenching smaller pieces in oil. It will be explained in the next

[1] The name "troostite" was selected by Osmond in honor of the French chemist Troost.

[2] A colloid may be regarded as a substance passing from the state of solution to that of an aggregate or vice versa; it is no longer a solution but not yet an aggregate. To express it more scientifically, while not a true solution the particles of solvent and solute are ultra-microscopic. According to Le Chatelier so-called colloidal solutions are in no way solutions, but merely liquids holding in suspension very finely divided particles; the expression, he says, should not be used.

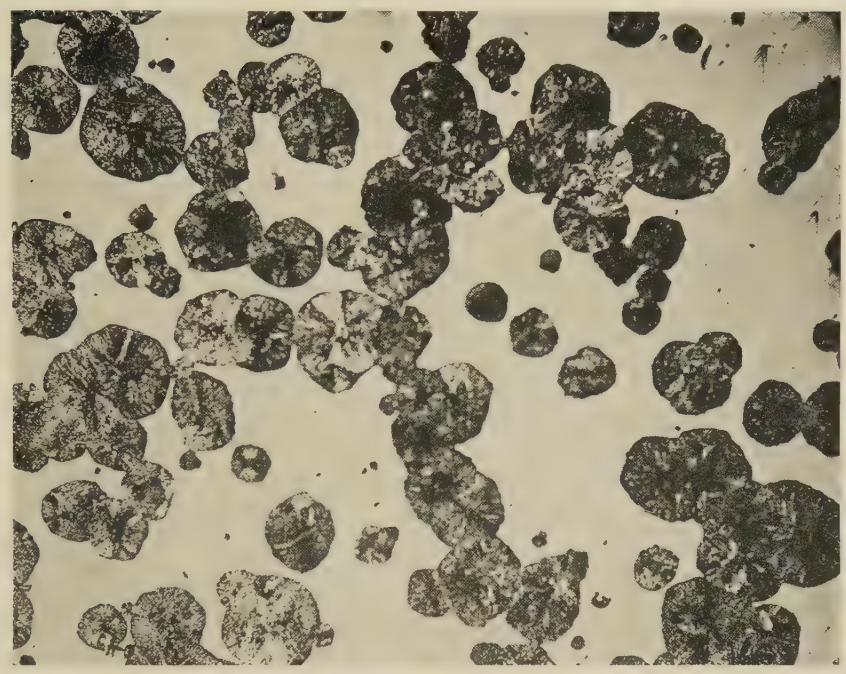


Fig. 201. — Troostite in steel containing 1.50 per cent carbon. Magnified 150 diameters.

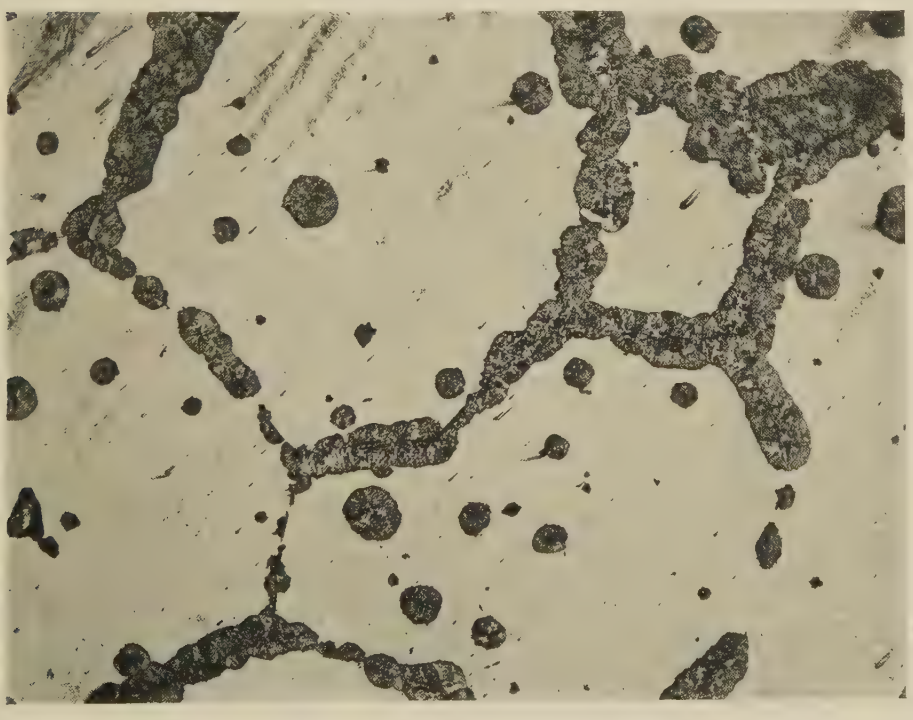


Fig. 202. — Troostite in steel containing 1.50 per cent carbon. Magnified 150 diameters.

chapter that troostite may also be produced by tempering (i.e. reheating below the critical range) austenitic and martensitic steels.

Troostite is readily produced by heating a bar of steel, containing 0.50 per cent carbon or more, white hot at one end and quenching it in water, when at some distance from the heated end the temperature must necessarily have been such as to produce troostite. This can generally be detected by means of a file, the martensitic

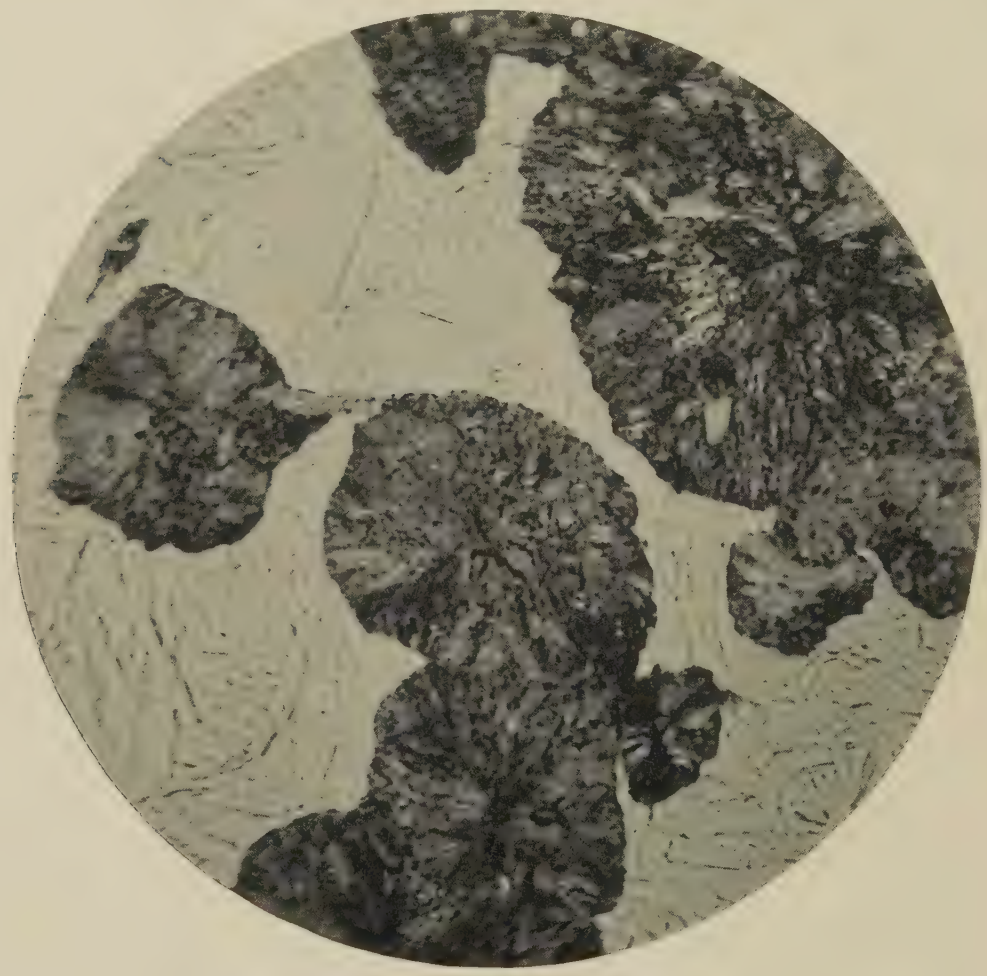


Fig. 203. — Martensite and troostite. Magnified 2690 diameters. Original magnification 3230 diameters. (F. F. Lucas.)

portion of the bar being too hard to be marked, while the troostitic part, although hard, can be scratched. The sorbitic and pearlitic portions are decidedly softer.

Properties of Troostite. — It will be obvious from the foregoing description of the nature and formation of troostite that its physical properties must be intermediate between those of martensite and of sorbite. For like carbon content troostite is softer and more ductile than martensite but harder and less ductile than sorbite. It will be shown that at some 400 deg. C. it begins to be transformed into sorbite.

Etching of Troostite. — Troostite is colored decidedly darker than any other constituent by the ordinary etching reagents. While dilute alcoholic solutions of nitric, picric, or hydrochloric acid yield satisfactory results, Kourbatoff's reagent is preferred by some.

Structure of Troostite. — Troostite generally occurs as dark-colored, irregular areas, representing sections through nodules generally accompanied by martensite or

Fig. 204. —Troostite and martensito-austenitic matrix in steel containing 1.50 per cent carbon. Magnified 150 diameters. (Boylston.)

sorbite or both, or as membranes surrounding martensite grains (Figs. 201 to 204). Osmond describes the structure of troostite as "almost amorphous, slightly granular, and mammillated." On deeper etching the martensitic structure of the matrix is generally revealed as shown in Figure 204. In hypo-eutectoid steel free ferrite, and in hyper-eutectoid steel free cementite, may also be present and, indeed, even well-developed pearlite. The steel shown in Figure 205 was quenched during its critical range and contains martensite (bright), troostite (dark), sorbite (lighter than troostite and ill-defined), and pearlite (laminated).

SORBITE

Sorbite is not, properly speaking, a constituent of hardened steel. It seems appropriate, however, to mention it again here, seeing that it constitutes the connecting link between annealed (pearlitic) steels and hardened (troostito-martensitic) steels, and also because it results from the transformation of troostite, thus completing the various stages assumed by iron-carbon alloys in passing from the condition of aus-

tenite, stable above the range, to that of pearlite, stable below the range. These stages are (1) austenite, (2) martensite, (3) troostite, (4) sorbite, and (5) pearlite.

Sorbite is now generally regarded as an uncoagulated mixture of the constituents of troostite and of pearlite; it apparently contains (1) some hardening carbon, i.e. carbon or Fe_3C in solution, hence the greater hardness and strength of sorbite compared to the hardness and strength of pearlite; (2) a considerable quantity of alpha iron, hence its magnetism and relative softness; and (3) a considerable quantity of crystallized Fe_3C (cement carbon) as proven by analysis. While sorbite is claimed by some to contain the same constituents as troostite it holds considerably less undecomposed solid solution and considerably more alpha iron, hence it is much softer and more ductile than troostite. In other words the transformation which eventually

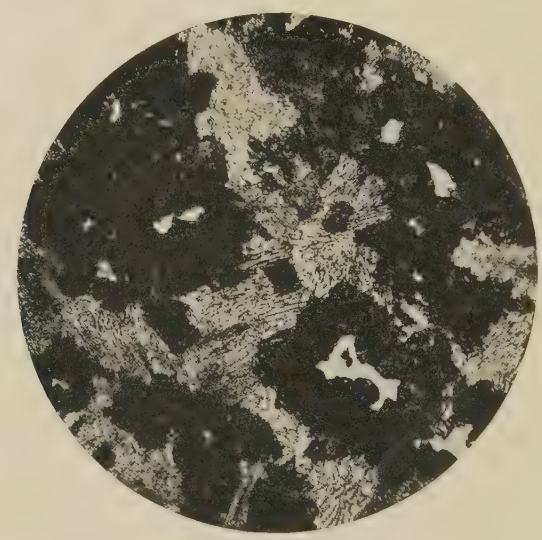


Fig. 205. — Steel. Carbon 0.80 per cent. Quenched in the critical range. Magnified 430 diameters. (Boylston.)

must lead to the formation of pearlite is more advanced in sorbite than it is in troostite. The nomenclature committee, already referred to, describes sorbite as follows: "Aggregate . . . In the transformation of austenite, the stage following troostite . . . and preceding pearlite. Most writers believe it essentially an uncoagulated conglomerate of irresoluble pearlite with ferrite in hypo- and cementite in hypereutectoid steels respectively."

The occurrence, etching, structure, and properties of sorbite have been described in Chapters XI, XII, and XIII, when it was shown that it is formed (1) in small pieces of steel cooling in the air from above their critical range, (2) in larger pieces quenched in oil from above the range, or (3) in small pieces quenched in water from near the bottom of the range. In other words to form sorbite we must so regulate the cooling through the critical range that it is allowed to form but prevented from further transformation (into pearlite). It will be seen in the next chapter that sorbite is also formed on tempering austenitic, martensitic, and troostitic steels.

By its physical properties sorbite occupies an intermediate position between

troostite and pearlite; as previously mentioned it is stronger, harder, and less ductile than pearlite but softer and more ductile than troostite.

Summary. — Austenite is believed to be a solid solution of carbon or of the carbide Fe_3C in gamma iron; martensite, a solid solution of carbon or of the carbide in alpha iron; troostite and sorbite, fine aggregates of the carbide and of alpha iron (ferrite); and pearlite, an aggregate of the same constituents in the form of well-defined lamellæ. There is generally no sharp line of demarcation indicated as existing between troostite and sorbite, although by their structural aspects they can be sharply differentiated. Microscopical examination does not give evidence of sorbite being *gradually* converted into troostite or vice versa, and it is reasonable to conclude that there exists greater difference between these two constituents than a mere difference in the fineness of their component parts, that is that troostite is simply a finer aggregate than sorbite. It is permissible to suspect a more critical dissimilarity. It is believed by some that in troostite the particles of ferrite and cementite are so very finely divided that this constituent partakes of the nature of colloids. Let us also bear in mind that it is far from conclusively established that the sorbite and troostite resulting from cooling steel at the required speed, that is formed at the A′r point, are identical in their nature and properties to the same constituents formed by reheating martensitic steel (tempering).

The nature of martensite and of troostite will be found further discussed in Chapter XVI under "Theories of Hardening."

Metarals and Aggregates. — Howe suggests dividing all microscopical constituents of iron and steel into (1) metarals and (2) aggregates.

These he describes as follows: "Metarals, true phases like the minerals of nature. These are like definite chemical compounds, or solid solutions, and hence consisting of definite substances in varying proportions. . . . Aggregates, like the petrographic entities as distinguished from the true minerals. These mixtures may be in definite proportions, i.e. eutectic or eutectoid mixtures (ledeburite, pearlite, steadite) or in indefinite proportions (troostite, sorbite)." [1] Under these two headings the constituents of iron-carbon alloys would be classified as follows:

Metarals: ferrite, cementite, austenite, graphite.

Aggregates: pearlite, sorbite, troostite, ledeburite, steadite.

Should we admit the existence of solid colloidal solutions, it is not clear whether these should be grouped with the metarals or should form a distinct class between the metarals and the aggregates.

Hardening Eutectoid Steel. — It will now be profitable to consider separately the hardening of eutectoid, hyper-eutectoid, and hypo-eutectoid steel. In hardening eutectoid steel the metal should be heated through its critical range, i.e. through its single critical point $Ac_{3\text{-}2\text{-}1}$. By so doing we confer upon it full hardening power and finest possible structure. The steel should then be cooled from that temperature as promptly as possible, avoiding heating much above the range or long exposure at any temperature above the range, as either procedure would tend to increase the grain size of the metal. A temperature of some 775 to 825 deg. C. will generally be, there-

[1] Howe further writes: "Many true minerals, such as mica, felspar, and hornblende, are divisible into several different species. Such minerals are definite chemical compounds, in which one element may replace another. Others, such as obsidian, are solid solutions in varying proportions and in these also one element may replace another. Metarals like minerals differ from aggregates in being severally chemically homogeneous."

fore, the best temperature to which to heat and from which to cool eutectoid steel for the purpose of hardening. By this treatment the steel passes from a finely austenitic to a finely martensitic or troostito-martensitic condition.

Hardening Hyper-Eutectoid Steel. — Let us assume a steel containing 1.25 per cent carbon and, therefore, composed approximately of 94 per cent of pearlite and 6 per cent of free cementite. Upon heating this steel through its lower point $Ac_{3\cdot2\cdot1}$

Fig. 206. — Steel. Carbon 1.10 per cent. Magnified 100 diameters. Quenched in water from above its critical range. (Boylston.)

its 94 per cent of pearlite is converted into 94 per cent of austenite possessing hardening power, but the metal still contains 6 per cent of free cementite deprived of hardening power. If we heat it past its upper point Ac_{cm} the free cementite is absorbed and the whole mass becomes austenitic. A little reflection will show, however, that the steel should be quenched as soon as it rises above the point $Ac_{3\cdot2\cdot1}$, because we then produce, theoretically at least, 94 per cent of fine-grained martensite while retaining, to be sure, the original 6 per cent of cementite; but as this constituent is harder than martensite its presence adds to, rather than takes away from, the hardness of the quenched metal. Should we, on the contrary, heat to above Ac_{cm} before quenching, the whole mass would be converted into martensite, but it would be less hard if anything than the metal quenched at a lower temperature while its structure would be coarser and the danger of cracking the objects in the quenching bath would be greater. The best hardening temperature for hyper-eutectoid steels, therefore, is the same as that for eutectoid steel, namely, some 775 to 825 deg. C.

The following treatment has been described for hardening hyper-eutectoid steel: Heat above A_{cm} to cause the absorption of the free cementite and cool in boiling water or lead, thereby preventing the excess cementite from re-forming, although the quenching is too mild to produce cracks or serious distortion; the piece then should be reheated slightly above Ac_1 and quenched in the usual way.

The structure of a properly hardened hyper-eutectoid steel is shown in Figure 206. Like hardened eutectoid steel it consists of very fine martensite.

Hardening Hypo-Eutectoid Steel. — Let us take a steel containing some 0.50 per cent carbon and exhibiting therefore the points A_1 and $A_{3\cdot2}$. Such steel is made up of 58.5 per cent of pearlite and 41.5 per cent free ferrite. Upon heating it through its Ac_1 point the pearlite is converted into austenite, so that at this temperature some 58 per cent of the mass of the metal is endowed with hardening power. Should we quench this steel, therefore, as soon as it rises above its lower critical point but 58 per cent of its bulk would be hardened; it would still retain 42 per cent of soft ferrite.

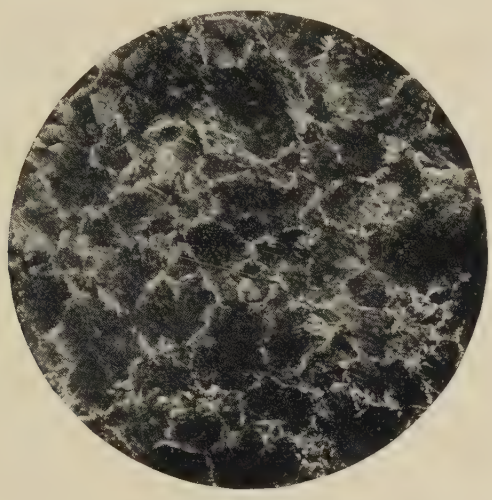


Fig. 207. — Steel. About 0.25 per cent carbon. Heated to 1000 deg. C. and quenched in water. Magnified 100 diameters. (W. B. Byers, in the author's laboratory.)

If, on the contrary, the heating be carried to just above $Ac_{3\cdot2}$ the free ferrite is absorbed by the austenite and the whole mass becomes *hardenable*. Upon quenching the steel from that temperature its entire bulk may be converted into martensite or troostito-martensite, according to rate of cooling. While this martensite will not be quite so hard as the martensite produced by quenching from just above Ac_1 the metal as a whole will be harder and of a more uniform and finer structure because of the absence of free ferrite, or at least of any considerable amount of it. It follows from these considerations that for the purpose of hardening, hypo-eutectoid steel should be quenched from just above its upper critical point, namely, $Ac_{3\cdot2}$ or Ac_3 (825 to 925 deg. C. according to carbon content). Hypo-eutectoid steel containing very little carbon, say less than 0.25 per cent, cannot be very materially hardened by the ordinary quenching methods because of the large amount of soft ferrite which it contains in excess of the eutectoid ratio and which cannot be retained in solution, even on very quick cooling (see Chapter XIII, Fig. 172). The structure of steel containing about 0.25 per cent carbon and quenched in water is shown in Figure 207.

CHAPTER XV

THE TEMPERING OF HARDENED STEEL

TROOSTITIZING AND SORBITIZING

The hardening treatment described in the preceding chapter, if properly conducted, imparts to the steel (1) the smallest possible grain, (2) maximum hardness, (3) maximum tensile strength, (4) minimum ductility, and (5) produces internal strains.

In its hardened condition, steel is often harder than necessary, and generally too brittle and too severely strained for most purposes.

In order to relieve the strains, decrease the brittleness, restore some ductility while preserving sufficient hardness and strength, the metal is generally "tempered." The operation is called "tempering" because it somewhat mitigates, or tempers, the effects of the previous hardening treatment. It is also called "drawing," or "drawing the temper."

Tempering Operation. — The tempering operation consists in heating hardened and therefore martensitic steel, or, in the author's opinion, austenito-troostitic steel, into a range of temperature which extends from room temperature to the Ac_1 critical point.

When it is desired to retain great hardness, necessarily combined with little ductility, the tempering temperature does not exceed 400 deg. C., but when it is desired to retain great strength only, and at the same time secure considerable ductility, the tempering is conducted above 400 deg. C. and may be as high as 700 deg. C. It will soon be seen that the former is essentially a troostitizing treatment, the latter a sorbitizing treatment. It is to be deplored that the same term "tempering" is applied to those two treatments, seeing that their aims are so widely different. It would be a happy solution if metallurgists could agree to reserve the term "tempering" for the reheating of hardened steel below 400 deg. C. and the term "drawing" for the reheating above 400 deg. C.

In the following description, the tempering of steel will be considered under two headings: (1) tempering for hardness, or troostitizing; (2) tempering for strength and ductility, or sorbitizing.

Explanation of the Tempering of Steel. — Hardened steel is generally considered to be in an unstable or metastable condition and, therefore, eager to return to a more stable form and actually undergoing this change whenever given an opportunity, that is on raising its temperature. At room temperature the passage of an unstable martensitic condition into a more stable troostitic or sorbitic form is prevented by the rigidity of the metal. A slight heating, however, produces some plasticity and such transformation takes place to a small extent. On increasing the temperature the rigidity diminishes further and the transformation advances. It will be seen that at some 600 deg. C. the metal assumes a stable condition, i.e. is fully tempered or drawn.

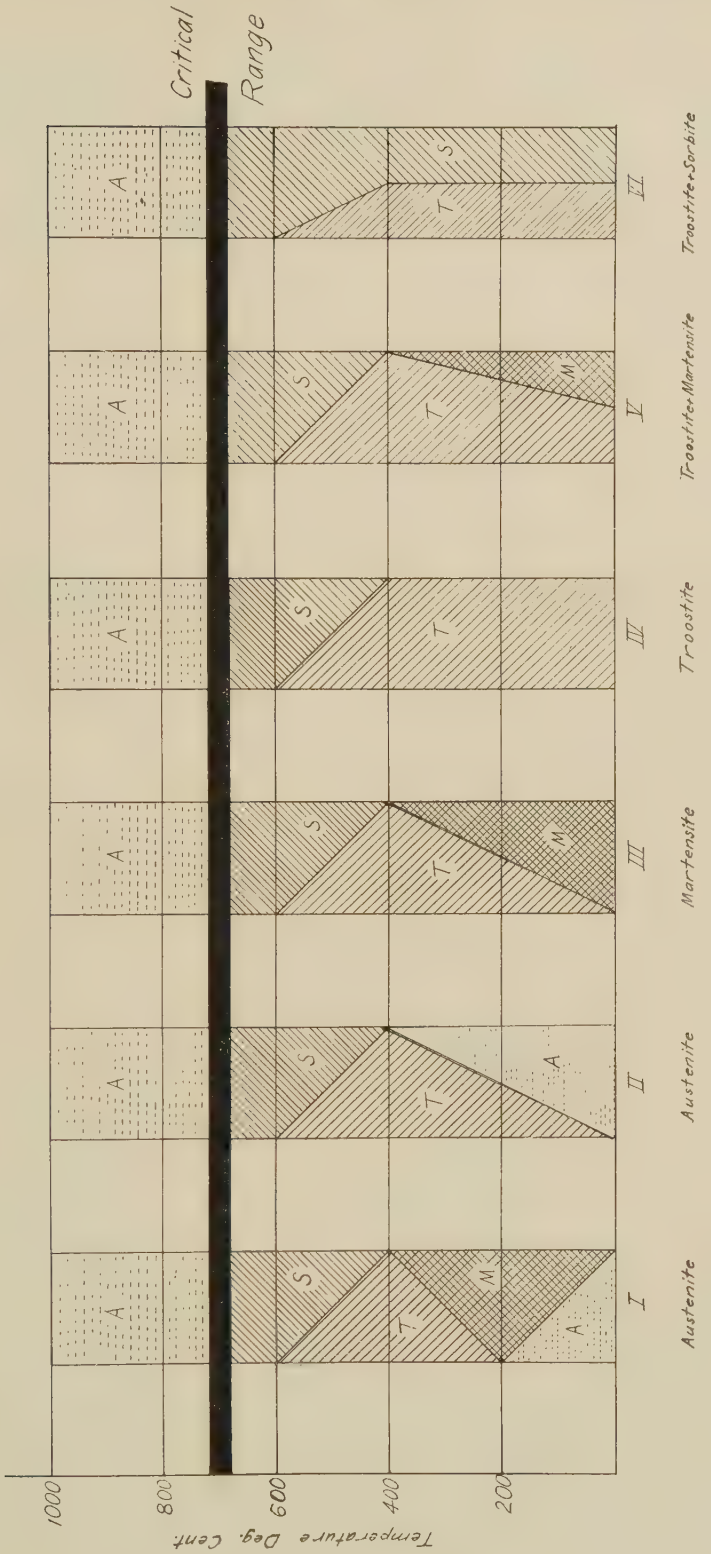


Diagram depicting the tempering of Hardened Steel.

Fig. 208.

Structural Changes Induced by Tempering. — To understand the rationale of the tempering operation, it is essential that we should know what structural changes result from heating hardened (martensitic) steel to temperatures ranging from room temperature to the Ac_1 point. An attempt has been made to show these changes

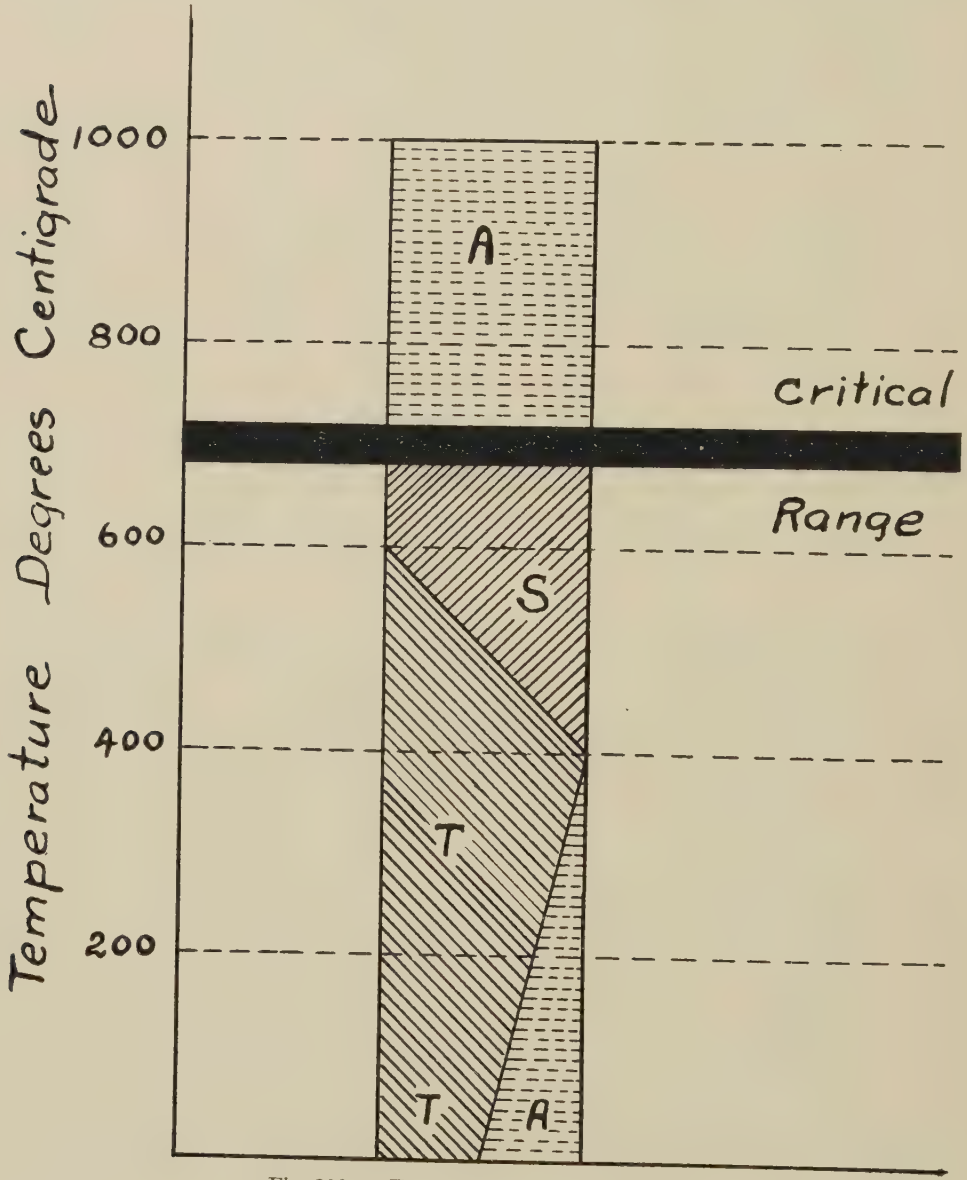


Fig. 209. — Tempering of hardened steel.

diagrammatically in Figure 208 on the general assumption that martensite is a solid solution of carbon or of the carbide Fe_3C in alpha iron, and in Figure 209 according to the author's belief that hardened steel is an aggregate of austenite and troostite. Were it possible to retain by very rapid cooling carbon steel untransformed, it would remain austenitic, and we may first consider the structural change likely to occur in

this unstable austenite on heating it above room temperature. At that temperature the rigidity of the metal is so great that a return to a more stable form is not possible but, on heating it very slightly, sufficient plasticity is produced to permit a partial transformation of austenite. This partial transformation, theoretically at least, should result in the formation of martensite, troostite, and sorbite in the order named as the tempering temperature increases. This has been depicted in I, Figure 208. In this diagram it is shown (1) that as soon as austenite is heated above atmospheric temperature it begins to be converted, in accordance with common belief, into martensite, (2) that it is entirely converted into martensite at 200 deg. C., (3) that in heating above 200 deg. martensite begins to pass to troostite, (4) that at 400 deg. the transformation of martensite into troostite is complete, (5) that above 400 deg. troostite is gradually converted into sorbite, (6) that at 600 deg. C. the transformation of troostite into sorbite is complete, and (7) that the sorbite condition is the final condition acquired by hardened steel when reheated close to, but below, its critical range. While it is certain that lamellar, i.e. true, pearlite cannot be formed by reheating hardened steel below its critical range, it will be shown (Chapter XVII) that long heating of sorbite near the critical range, that is between 600 and 700 deg. C., results in the formation of granular pearlite brought about by the spheroidizing of the cementite. The tempering of austenite depicted in I, Figure 208, represents the transformation which, according to theoretical consideration, should be expected to take place. Some observers, however, report that on tempering austenite it is at once converted into troostite as soon as the rigidity of the steel has been sufficiently relaxed, the martensitic stage not being assumed. This is shown diagrammatically in II, Figure 208. Here, again, it is indicated that at 400 deg. the steel is entirely troostitic and at 600 deg. entirely sorbitic. Benedicks thinks that it is quite possible that austenite is first transformed into martensite but that the resulting martensite is so readily and quickly converted into troostite that its short existence easily escapes observation. His belief is based upon the following considerations: (1) the austenite retained in high carbon steel by very sudden cooling is subjected to great pressure caused by the accompanying martensite having been formed with considerable dilatation; (2) on reheating this martensito-austenitic steel the martensite is first converted into troostite, because this transformation taking place with contraction is readily induced; (3) once this transformation is started, the pressure upon the austenite is released and this constituent, in turn, passes first to the martensitic stage (with increase of volume) and then quickly to the troostitic stage (with decrease of volume), the martensitic condition being of so short duration as to escape detection readily.

It has been shown that martensite is generally present in commercially hardened steel. Since this constituent represents a partial transformation of austenite it follows that it must be more stable than austenite at room temperature. It is sufficiently unstable, however, to be readily converted first into troostite and then into sorbite on tempering, as indicated in III, Figure 208. At 400 deg. the transformation of martensite into troostite is complete, while at 600 deg. troostite is replaced by sorbite. Bearing in mind the physical properties of martensite, troostite, and sorbite, it will be readily understood why, on tempering martensitic steel, its hardness gradually decreases while it becomes less brittle and indeed quite ductile if made sorbitic.

Commercially hardened steel frequently contains large proportions of troostite. The tempering of troostite is depicted in IV, Figure 208. This constituent being decidedly less unstable than martensite requires greater plasticity, i.e. a higher tem-

perature, before being transformed into a still more stable condition. Experimental evidences seem to show that the tempering of troostite, i.e. its transformation into sorbite, requires a temperature of at least 400 deg. and that at 600 deg. the transformation is complete. Since in practice the tempering of steel is seldom carried above 300 deg. it would seem as if steels made up of troostite do not need to be tempered, being sufficiently tough. There seems to be no reason to doubt the accuracy of the

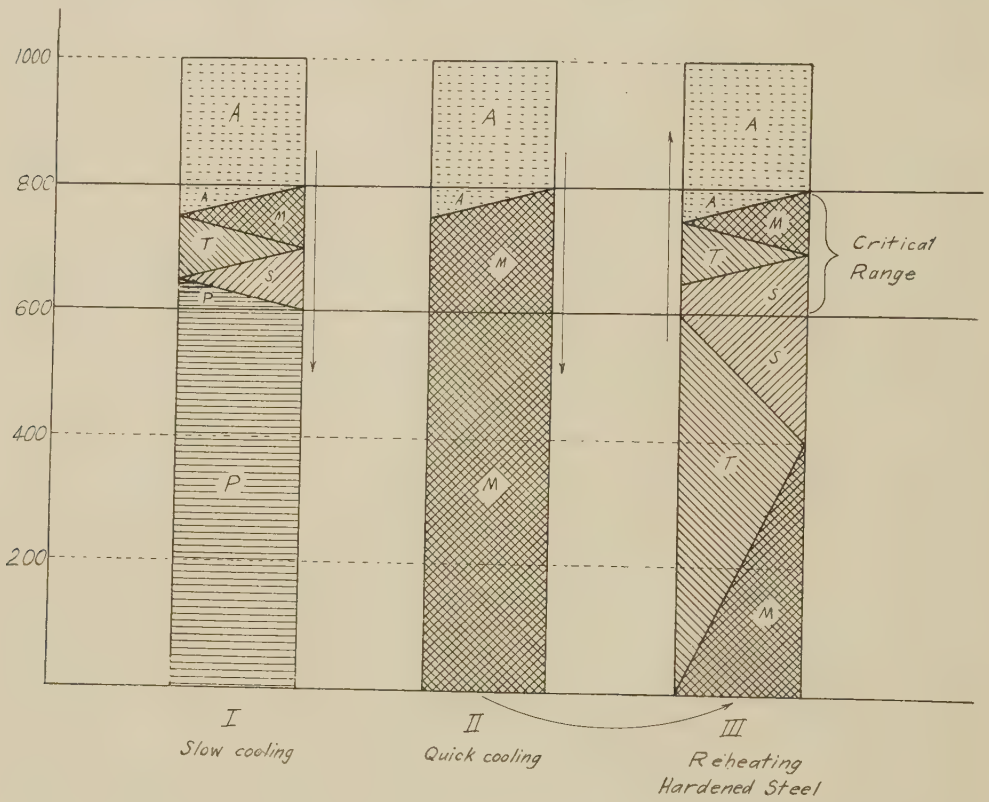


Fig. 210. — Diagram depicting the constituents formed (I) on slow cooling, (II) on quick cooling, and (III) on reheating hardened steel.

above inference. Commercially hardened steels, however, are generally in need of tempering because of the large proportion of the excessively hard and brittle martensite they usually contain.

In V, Figure 208, the tempering of hardened steel containing both martensite and troostite has been depicted. It is assumed that the martensite present begins to be converted into troostite as soon as the temperature of the metal rises, while the transformation of the troostite into sorbite begins only at 400 deg.

From the diagram used to illustrate the tempering of steel it will be apparent that sorbite is relatively so stable a constituent that its transformation into pearlite cannot be effected below the critical range or, in other words, that it cannot be tempered. Indeed sorbitic steels not being hardened steels need not be considered in connection with the tempering operation. A graphical representation of the tempering of troostito-sorbitic steel, however, has been included in Figure 208. It shows that such steel remains unchanged until its temperature reaches 400 deg., when the troostite it contains

begins to be transformed into sorbite, the transformation being, as usual, complete at 600 deg.

In Figure 209 hardened steel is assumed to be an aggregate of austenite and troostite. On tempering, the austenite transforms into troostite, the transformation being complete at 400 deg. C. This view is explained in the following chapter.

Osmondite. — It has been shown that on tempering hardened steel it is entirely converted into troostite at about 400 deg. C. Below that temperature some martensite remains in the structure, or in the author's opinion some austenite, while above it some sorbite is present. To the condition of steel when made up wholly of troostite Heyn gave the name of "osmondite."

Troostite is more readily colored by the usual etching reagents than any other constituent of steel, from which it follows that steel made up exclusively of troostite, i.e. in the osmondite condition, must exhibit maximum coloration. Again Heyn has shown that the solubility of steel in dilute sulphuric acid increases with the amount of troostite present, being maximum in steel tempered to about 400 deg. C. From these observations Heyn described osmondite as a constituent of steel characterized by maximum solubility in acids and by maximum coloration under the action of acid metallographic reagents. In the report of the Committee on the Nomenclature of the Constituents of Iron and Steel of the International Association for Testing Materials osmondite is described as follows: "Probably aggregate. That stage in the transformation of austenite at which the solubility in dilute sulphuric acid reaches its maximum rapidity. Arbitrarily taken as the boundary between troostite and sorbite. . . . The following hypotheses have been suggested, none of which has substantial experimental foundation: (1) A solid solution of carbon or an iron carbide in alpha iron; (2) The colloidal system of Benedicks in its purity, troostite being this system while forming at the expense of martensite, and sorbite being this system coagulating and passing into pearlite; (3) The stage of maximum purity of amorphous alpha iron in the way to crystallizing into ferrite."

Structural Changes on Slow Cooling, Quick Cooling, and Reheating. — It seems helpful and instructive to depict graphically in a single diagram the structural changes taking place in eutectoid steel (1) on slow cooling through its critical range, (2) on quick cooling through that range, and (3) on reheating quickly cooled (hardened) steel above the range. The changes indicated in I (Fig. 210) show, as already explained, that steel, on cooling slowly through the critical range, is converted successively into martensite, troostite, sorbite, and pearlite, bearing in mind, however, that some believe it to be converted directly into pearlite, a view which is not well supported either by experimental evidence or theoretical reasoning. On heating the same steel from below to above the range the same changes would take place but in the reverse order. In II the steel has been cooled at such speed that martensite was formed but prevented from further transformation, hardened martensitic steel being produced. The reheating of this martensitic steel is depicted in III. Below the range martensite is gradually converted first into troostite and then into sorbite. On entering the range the steel remains sorbitic but on further heating the sorbite is converted back into troostite and then into martensite. Near the top of the range austenite begins forming, the transformation being complete as the steel emerges from its range. Similar structural transformations would take place in subjecting hypo-eutectoid and hyper-eutectoid steels to like treatments, but free ferrite or free cementite would generally be present.

Assuming martensite to be an aggregate of austenite and troostite, the diagram should be modified as shown in Figure 211.

Microstructure of Hardened and Tempered Steel. — The structural changes corresponding to the transformations taking place on tempering hardened steel described in the foregoing pages are not always readily detected by microscopical examination. This is due to the fact that, structurally speaking, these changes are often pseudomorphic changes, the crystalline forms of the original constituent or

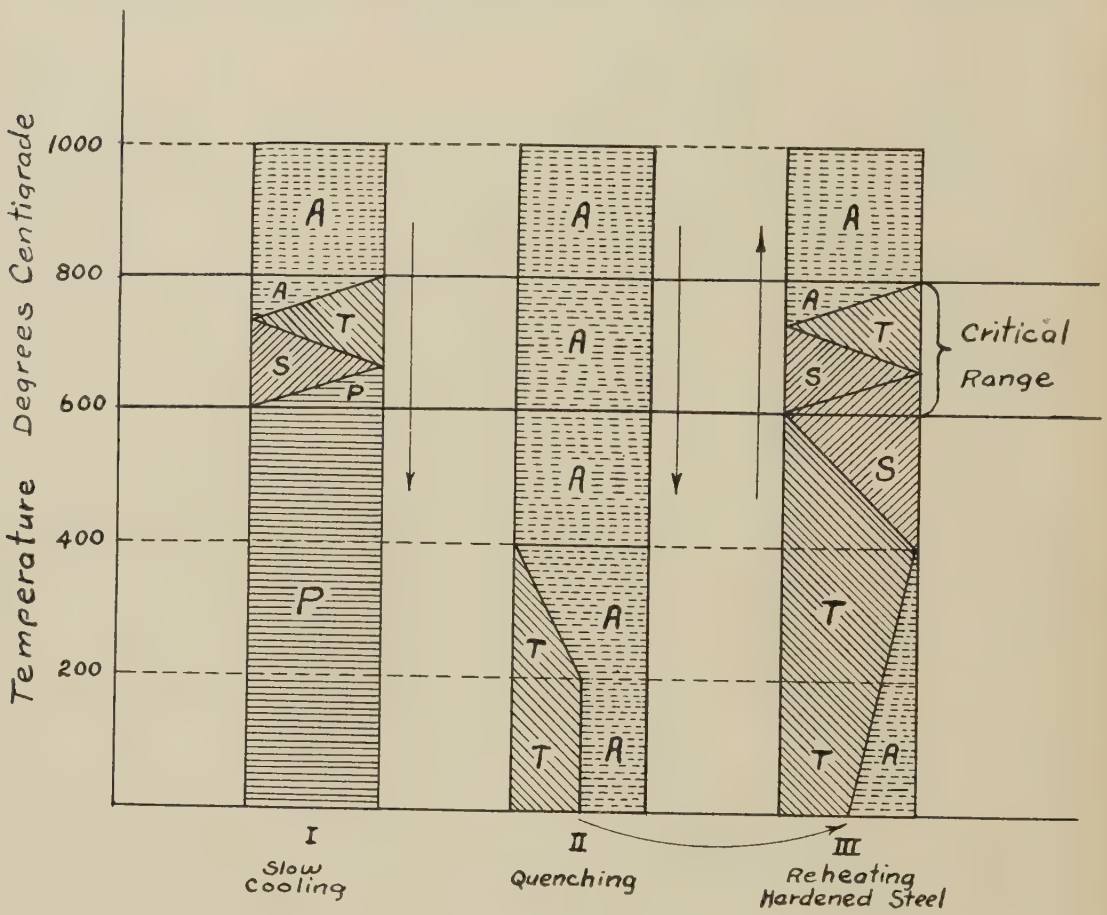


Fig. 211.

constituents having been retained, although the nature of the crystals themselves has been altered.

Referring to pseudomorphism Dana writes: "The crystalline forms under which a species occur are sometimes those of another species." Bayley defines pseudomorphs as bodies possessing forms borrowed from another substance, or as a body possessing the form of one substance and the chemical and physical properties of another. In the formation of a pseudomorph the material of the original substance is replaced by the new substance but its external form remains unchanged.

According to Heyn the following appearances are observed in the case of eutectoid steel:

(1) After hardening but before tempering: martensite with well-developed needles remaining uncolored after an immersion of 10 minutes in a solution of 1 per cent of hydrochloric acid in alcohol.

(2) After tempering between 100 and 200 deg.: martensitic structure unchanged but colored yellow or brown.

(3) After tempering to 275 deg.: the needle structure becomes coarser and recalls mixtures of austenite and martensite, one of the constituents remaining uncolored, the other assuming a dark coloration.

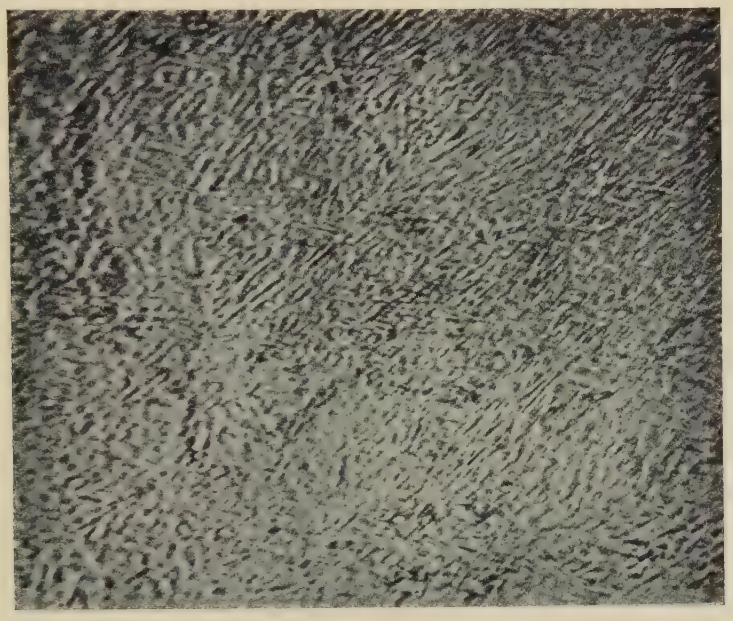


Fig. 212. — Steel. Carbon 0.45 per cent. Magnified 1000 diameters. Heated to 825 deg. C., quenched from 720 deg., and tempered between blue and brown (275 deg.?). (Osmond.)

(4) After tempering to 405 deg.: the needles have disappeared and the sample appears dark and mottled, suggesting a mixture of two relatively dark constituents; this is troostite.

(5) After tempering to 500 deg.: the light areas become more abundant.

(6) After tempering to 600 deg.: irregular meshes are observed rounded and light, partially surrounded by a darker network which appears to stand in relief.

Photomicrographs of the structure of hardened and tempered steels are reproduced in Figures 212 and 213. Others taken under very high magnification by Lucas are described in the following chapter, and clearly show the transformation of austenite into troostite.

Tempering Temperatures. — The effect of tempering begins to be noticeable at about 100 deg. C. and increases in intensity as the temperature rises, until finally at some 600 deg. the hardness resulting from hardening may have been practically obliterated. The temperature to which hardened steel should be heated for tempering varies, therefore, with the use to which it is destined. If it is desired to retain the greatest possible hardness, necessarily with its accompanying brittleness, the steel

should be reheated but slightly above 200 deg. C., as, for instance, in tempering razor blades, when extreme hardness is essential and brittleness relatively immaterial. If, on the contrary, considerable toughness is indispensable, at the necessary sacrifice of some hardness the steel should be tempered to some 300 deg. C. or even to a higher temperature. The great majority of tools are tempered between 200 and 300 deg.

Tempering Colors. — Hardened steel objects subjected to tempering being generally heated in an oxidizing atmosphere, very thin films of oxides form upon their surfaces. The colors of these films vary with the temperature, that is, to each tempering temperature corresponds a certain color, and blacksmiths generally depend

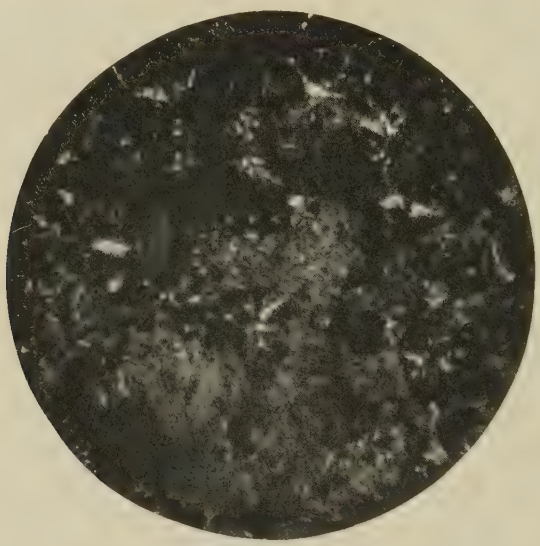


Fig. 213. — Steel. Carbon 0.50 per cent. Magnified 500 diameters. Heated to 850 deg. C., quenched in water, reheated to 400 deg., and quenched in water. (W. H. Knight, in the author's laboratory.)

upon these colors for the tempering of their tools, the use of pyrometers for this operation being far from general. According to Howe the tempering colors and corresponding temperatures are as follows:

Pale yellow	220 deg. C. or	428 deg. F.
Straw	230 " " "	446 " "
Golden yellow	243 " " "	469 " "
Brown	255 " " "	491 " "
Brown dappled with purple	265 " " "	509 " "
Purple	277 " " "	531 " "
Bright blue	288 " " "	550 " "
Pale blue	297 " " "	567 " "
Dark blue	316 " " "	600 " "

In order that the tempering colors may be plainly seen the steel objects should be smooth and bright, preferably polished.

Time at Tempering Temperature. — It is sometimes stated that once the desired temperature is obtained, as indicated by the color, little is to be gained by maintain-

ing the steel at that temperature any length of time on the ground that it will not result in producing additional tempering. The tempering of steel has been compared to the releasing of a spring permitting a certain structural rearrangement, that is, a certain tempering of the metal, but not more, at any temperature. To produce additional tempering the temperature must be increased, that is, the spring must be further released. It has been shown, however, that the maintenance of hardened steel at a certain tempering temperature often does produce additional tempering effect. It was further ascertained that the color, instead of remaining unchanged at any given temperature, advances in the tempering color scale as it would with increasing temperature. In other words, the tempering colors, contrary to the view sometimes held, are not an absolute criterion by which to judge of the temperature of the steel, since they vary with the length of time during which the steel is kept at any temperature. These experiments seem to show, however, that the amount of tempering effected is closely related to the color, that is, that to each shade corresponds a certain amount of tempering. It should, however, be borne in mind that these colors, with the corresponding tempering they imply, may be obtained in two ways: (1) through short exposure at a certain temperature and (2) through longer exposure at lower temperatures. The same amount of tempering, for instance, would result (*a*) from heating hardened steel to 288 deg., when its color is bright blue, followed by immediate cooling, and (*b*) from heating it to 255 deg., when its color is brown, and maintaining it at that temperature until its color becomes bright blue. Unless baths kept at constant temperatures are used, however, it is evident that in practice the steel should be quenched as soon as the desired color is produced and while its temperature is rising, because it is simpler and more convenient to produce that color on a rising temperature than by maintaining the metal at a constant temperature.

Some writers doubt the existence of so close a relation between the color and the resulting tempering. According to Barus and Strouhal, to each tempering temperature corresponds a maximum tempering effect, which is the more quickly reached the higher the temperature. At 100 deg., for instance, the maximum effect was not obtained after one hour, although maintaining the steel at that temperature two more hours had but little additional effect. At 200 deg. the maximum effect was obtained in ten minutes, while at 300 deg. one minute was sufficient.

Mathews tempered three hardened pieces of the same steel in a salt bath at 422 deg. C., keeping them at that temperature respectively for 8, 20, and 40 minutes and obtained Brinell hardness numbers of 425, 390, and 340 respectively.

Rate of Cooling from Tempering Temperature. — Once the desired amount of tempering is effected, as indicated by the color or otherwise, it would seem as if the rate of cooling to atmospheric temperature would be quite immaterial. In troostitizing the piece is generally quenched, merely for convenience. The theory is that while by keeping the metal at a certain temperature its tempering may be carried farther, on cooling tempering ceases, for the spring is now tightened, to use the simile already referred to, so that the rate of cooling is without influence. In sorbitizing, however, in the case of some alloy steels at least, slow cooling from the tempering temperature may result in great fragility under shock, which is sometimes referred to as "blue brittleness." Such steels should be quenched in tempering.

Hardening and Tempering Combined. — A method of hardening and tempering combined, frequently employed when but one end of a tool must be hardened, con-

sists in heating the tool above its critical range, quenching that portion only which is to be hard, removing it from the bath, and allowing the heat stored in the unquenched portion to heat by conduction the quenched part until the desired temper color is obtained, when it is again quenched lest the tempering be carried too far.

Carbon Condition in Tempered Steel. — It is generally admitted that the combined carbon present in steel may exist under two different conditions: (1) as hardening carbon, that is as carbon or the carbide Fe_3C *dissolved* in iron, and (2) as cement carbon, that is as the *crystallized* carbide Fe_3C or cementite. It is further believed (*a*) that pearlite is quite, if not altogether, free from hardening carbon, (*b*) that martensite contains, for a given steel, the maximum amount of hardening carbon that can be produced and retained in that steel by the ordinary hardening operation, and (*c*) that on tempering martensite the amount of hardening carbon decreases as the tempering temperature increases, while the proportion of cement carbon increases correspondingly. Heyn, however, found that on analyzing the residue remaining on dissolving, in dilute sulphuric acid, hardened eutectoid steel tempered below 400 deg., it contained no carbon in the form of the carbide Fe_3C, that is no cement carbon. For the carbon remaining in the residue and which, in his opinion, is different from cement carbon, Heyn suggested the notation Cf. Not until a temperature of 400 deg. had been reached on tempering was cement carbon detected in the residue. Heyn infers from these observations (1) that troostite contains no cement carbon, its residual carbon being in the hypothetical Cf condition, (2) that osmondite contains the maximum amount of Cf carbon, and (3) that sorbite must be formed, that is, the steel must be tempered above 400 deg. in order to produce cement carbon. Heyn further argues that the deep coloration produced on etching hardened and tempered steel is caused by the separation of Cf carbon, being, therefore, maximum in osmondite, that is, when the steel contains nothing but troostite.

Osmond very appropriately remarks that it is not necessary in order to explain Heyn's results to admit the existence of a new form of carbon, it being quite possible that the Cf carbon of Heyn is cement carbon, that is, Fe_3C so finely divided when formed below 400 deg. that it is readily decomposed by the acid, while above 400 it becomes coarser and, therefore, resists better the action of the acid.

Decrease of Hardness on Tempering. — According to Boynton the decrease of hardness taking place on tempering is gradual up to 350 deg., quite sudden between 350 and 550 deg., and nil above 550 deg.

Heyn found the following values for the loss of hardness on tempering expressed in per cent of the original increase produced by the hardening operation:

At 100 deg.	2.5 per cent	At 400 deg.	70.0 per cent
" 200 "	14.0 " "	" 500 "	87.5 " "
" 300 "	41.0 " "	" 600 "	97.5 " "

Heyn also observed that the loss of hardness takes place most quickly at 300 deg.

Heat Liberated on Tempering. — In hardening steel the cooling through and below its critical range is so rapid that the transformation of austenite which would have taken place had time been given can proceed but partially. The heat which would have been generated had the transformation been complete remains latent in hardened steel. On tempering, however, the partially suppressed transformation is permitted to proceed farther, this return to a more stable condition being accompanied by some evolution of heat. According to Osmond this latent heat can be made ap-

parent by dissolving hardened steel in double chloride of ammonium and copper, when it evolves more heat than unhardened steel.

Heyn made some careful determinations of the heat generated on tempering hardened steel. The greater acceleration in heating hardened steel was made apparent by the differential method, using as neutral bodies similar steels in their pearlitic, that is unhardened, condition. It was observed that the heat generated on tempering is maximum at 360 deg.

H. Schottky reports that when placing hardened steel in water vapor its temperature rises several tenths of a degree above that of the vapor, from which it must be

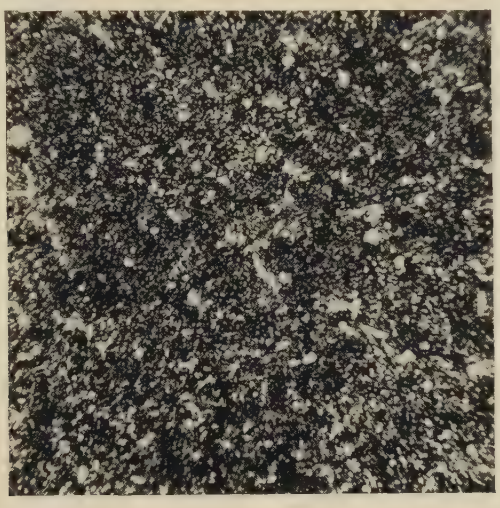


Fig. 214. — Steel. 1.25 per cent carbon. Heated to 800 deg. C., quenched in oil, reheated to 600 deg. C., cooled in air. Magnified 675 diameters. (E. L. Reed, in the author's laboratory.)

inferred that even at so low a temperature some tempering must take place. He finds that the evolution of heat increases with the carbon content up to a certain maximum and then decreases. The following results were obtained:

Carbon per Cent	Quenching Temp. Deg. C.	Temperature of Steel Pieces
0.54	1000	100.15
0.89	1100	100.35
1.22	1000	100.55
1.34	1300	100.33
1.10	1350	100.20

Changes of Volume in Tempering. — When hardened steel is tempered it first contracts. This may be ascribed to the precipitation of some carbide. On further heating it expands, due to the transformation of austenite into more bulky martensite or troostite.

Tempering for Hardness or Troostitizing. — When it is desired to retain in the finished articles (cutting tools, for instance) the major part of the hardness produced by quenching, necessarily combined with little ductility, the steel should be heated

according to requirements to temperatures varying generally from 100 to some 400 deg. C. This results in the transformation of some fine-grained martensite into fine-grained troostite, hence the treatment may be rightly described as troostitizing. It is understood that the higher the tempering temperature, the greater the loss of hardness, and the less the brittleness.

Tempering for Strength and Ductility, or Sorbitizing. — When it is desired to retain the fine-grained structure of martensite combined with a major portion of the great strength of that constituent, and at the same time secure ductility, the martensitic steel should be heated according to requirements to temperatures extending from 400 to some 650 or even 700 deg. C., it being understood that the higher the tempering temperature, the greater the ductility and the less the strength. The treatment consists in transforming some of the fine-grained martensite, or the whole of it, into fine-grained sorbite, hence it may be described as a sorbitizing treatment, thereby differentiating it sharply from the tempering of hardened steel where great hardness must be retained, essentially a troostitic treatment. So-called "heat treated" articles have generally been subjected to this double treatment, namely hardening or martensitizing, followed by drawing or sorbitizing. The fine sorbitic structure thus obtained is shown in Figure 214.

CHAPTER XVI

THEORIES OF THE HARDENING OF STEEL[1]

It would be futile and of doubtful profit to review at length the various hypotheses which have been advanced to explain the hardening of iron-carbon alloys resulting from rapid cooling from above the thermal critical range, that is, from a temperature range in which they are non-magnetic. For some thirty years this important question has been debated with a vigor which at times approached violence. The collective mental effort of several generations of metallurgists to supply a solution of the problem has been enormous and the experimental labor likewise of vast proportions. While the sponsors of the various theories may think they have demonstrated the accuracy of their views, this has been done only, it is feared, to their own satisfaction. A fully satisfactory explanation of the hardening of steel, so logical and well supported by evidence that it must of necessity be accepted by all, is still to be evolved.

The author concluded as follows a paper on "Metallography and the Hardening of Steel" presented at the International Engineering Congress in September, 1915, in San Francisco:

It will be obvious from the foregoing that the many recent attempts at arriving at a satisfactory explanation of the hardening of steel are based on one or more of the following conceptions: (1) existence of a hard allotropic variety of iron, (2) existence of solid solutions involving the occurrence of so-called "hardening" carbon, and (3) existence of strains in quenched steel causing or not an amorphous condition of the iron.

It will likewise be obvious that no theory so far presented fully satisfies our craving for a scientifically acceptable explanation of the many phenomena involved.

It would seem as if the methods used to date for the elucidation of this complex problem have yielded all they are capable of yielding and that further straining of these methods will only serve to confuse the issue, a point having been reached when this juggling, no matter how skillfully done, with allotropy, solid solutions, and strains is causing weariness without advancing the solution of the problem. The tendency of late has been to abandon the safer road of experimental facts and to enter the maze of excessive speculations, in which there is great danger of some becoming hopelessly lost.

The conclusion seems warranted that new avenues of approach must be found if we are ever to obtain a correct answer to this apparent enigma.

[1] A portion of this chapter has been taken from a paper by the author entitled "The Current Theories of the Hardening of Steel" presented at the February, 1926, meeting of the American Institute of Mining and Metallurgical Engineers.

In an effort to ascertain if possible the prevailing view of those best qualified to express an opinion, a questionnaire was submitted to the following gentlemen:

J. O. Arnold
Edgar C. Bain
Carl Benedicks
N. Belaiew
H. M. Boylston
Harry Brearley
G. K. Burgess
William Campbell
H. C. H. Carpenter
Pierre Chevenard
P. Dejean
C. A. Edwards
F. Giolliti
L. Grenet
Léon Guillet
Sir Robert Hadfield
W. H. Hatfield
Samuel L. Hoyt
Kôtarô Honda
Zay Jeffries
H. Le Chatelier
H. H. Lester
Francis F. Lucas
John A. Mathews
A. McCance
Albert Portevin
Walter Rosenhain
Bradley Stoughton
F. C. Thompson

The questions asked were:

1. What in your opinion is the nature of martensite and what causes its hardness?

2. What are the conditions necessary for its formation, and the mechanism of that formation?

3. If you believe it to be a solid solution of iron and carbon, or of iron and the carbide Fe_3C, what position do you think the carbon atoms or the carbide molecules occupy in the space lattices of the crystals?

4. What part, if any, do you think that strains play in the hardening of steel?

It is very gratifying to be able to report that 23 of the 29 eminent metallurgists consulted were good enough to reply, and I desire to place on record my sincere appreciation of their invaluable coöperation. The answers received from these gentlemen constitute an important symposium of the hardening theories.

Armed with the up-to-date information these answers brought him, the author proposes to discuss briefly, and as impartially and as clearly as he can, the phenomenon of the hardening of steel.

Austenite. — Since the hardening of steel is obviously due to a transformation of austenite into the condition existing in hardened steel, it seems advisable at the outset to recall the nature of that constituent. While austenite is quite universally believed to be a solid solution in which the iron is in the allotropic condition known as gamma, opinions differ as to the condition of the carbon dissolved in this gamma iron, some believing that the carbon is present in atomic dispersion, others that it exists as the carbide Fe_3C or cementite. From the answers received in regard to the condition of the carbon in martensite considered as a solid solution, soon to be discussed, it is warranted to conclude that a greater number of those consulted believe that carbon in austenite is present as carbide compared to the number of those who believe that it is present in atomic dispersion.

It is evident, however, that at the very outset of our inquiry we face a decided difference of opinion on a rather vital point, and that we must proceed by assuming that austenite is a solid solution of carbon or of the carbide Fe_3C in gamma iron.

Martensite. — The constituent found in hardened steel and to which it is believed the hardness of the steel is due has been called martensite. It generally occurs in the form of fine needles. Obviously those martensitic needles result from the transformation of austenite under certain conditions soon to be considered.

A sharp distinction should be made, however, between hardened (martensitic) steel and martensite because the former never consists exclusively of martensite. Hardened steel is an aggregate. It does necessarily contain martensite, and it is possible that it owes its hardness chiefly, if not wholly, to its presence, but it also contains one at least of the following constituents: undecomposed austenite, troostite, cementite, or ferrite. The author is not aware that the X-ray spectrum of martensitic steel has ever failed to reveal the presence of gamma lines, that is of austenite, while cementite lines very frequently occur. From the contention that martensite is a solid solution, hence a homogeneous phase, it would not follow, therefore, that hardened (martensitic) steel is a solid solution.

On the reasonable assumption that hardened steel owes a great part at least of its hardness to the presence of martensite, let us examine the evidences we have throwing light upon the nature of martensite and the conditions necessary for its formation.

Since martensite is obviously an alloy of iron and carbon we are naturally concerned with (1) the condition of the iron present in martensite; (2) the condition of the carbon present in martensite; and (3) the nature of the bond uniting the iron and the carbon. These are fundamental considerations and we shall not be able to proceed very far unless the questions involved can be satisfactorily answered.

Condition of Iron in Martensite. — We know that iron may exist in two at least, and some believe in three, allotropic forms: namely, gamma, beta, and alpha iron. The possible existence at a very high temperature of a fourth variety, delta iron, in steels containing less than 0.38 per cent carbon is not here considered as it has never been claimed that delta iron was present in martensite.

Assuming, then, the possible existence at room temperature of three allotropic forms of iron, there are seven mathematical possibilities in regard to the condition of iron in martensite as follows:

1. Gamma iron.
2. Beta iron.
3. Alpha iron.
4. Partly gamma and partly beta.
5. Partly gamma and partly alpha.
6. Partly beta and partly alpha.
7. Partly gamma, partly beta, and partly alpha.

It could easily be shown that these seven mathematical possibilities have been exhausted by metallurgists in their efforts to explain the nature of martensite. They could not go further than that. Most now believe, however, that beta iron has no real existence. Before crossing beta iron from our list, the author will again venture the opinion that its non-existence has never been satisfactorily demonstrated, the weapons employed consisting generally in arbitrarily worded definitions of allotropy.

If beta iron is left out, three possibilities only need be considered in regard to the conditions in which iron can be present in martensite, namely, (1) entirely in the gamma condition, (2) entirely in the alpha condition, or (3) partly in the gamma and partly in the alpha condition.

In order to proceed with our inquiry, we shall assume with the majority as evidenced from the answers received that in martensite, iron is present chiefly, at least,

in the alpha condition, bearing in mind, however, that some believe that martensite may also contain some gamma iron, that is some undecomposed austenite.

Some distinguish between fresh martensite and aged martensite. They tell us, however, that fresh martensite begins to age as soon as it is formed. After a few minutes it has reached middle life; after a few hours, old age. To study the properties of martensite in its infancy, therefore, one must act quickly. Moreover, the aging of martensite results in the precipitation of minute particles of cementite, which necessarily must transform it into an aggregate.

It is quite possible, in view of the rapidity with which martensite reaches maturity, that the X-ray analysis is too slow a process to reveal its true nature, as it may pass from babyhood to old age while its lattice structure is being studied. Whether, therefore, the spectrum of newly born martensite contains only alpha lines is not known and perhaps never can be known.

This precipitation of cementite from freshly produced martensite would, however, according to Jeffries, instead of softening it, increase its hardness up to a maximum corresponding to a so-called critical size of the cementite particles, further increase in size then producing decrease of hardness.

Condition of Carbon in Martensite. — We must now decide as to the condition in which carbon exists in martensite. It is generally held that one carbide of iron only, namely Fe_3C, need be considered, hence the carbon must be present either as carbon atoms or as molecules of the carbide.

A substantial majority of those consulted are inclined to believe that carbon is present in martensite in the form of the carbide Fe_3C.

Bond Uniting Iron and Carbon. — The third fundamental consideration deals with the nature of the bond uniting iron and carbon in martensite.

Martensite must of necessity be (1) a definite chemical compound, (2) a colloidal solution, (3) a solid solution, or (4) an aggregate.

One metallurgist, Arnold, has claimed that martensite was a definite chemical compound, namely, the carbide $Fe_{24}C$. He has had few followers and his hypothesis is generally held untenable. One at least of the gentlemen consulted, namely Grenet, considers the possibility of martensite being a colloidal solution when he writes: "This extreme fineness at which structural equilibrium ceases to be distinguishable from physico-chemical equilibrium characterizes, in my opinion, the colloidal state. And the term colloidal aggregate is better suited, I believe, to the aggregate designated as martensite than to the aggregates called troostite and sorbite."

While from the answers received it would seem as if it is quite generally held that martensite is a solid solution, many refer to the presence of gamma iron (undecomposed austenite?) and, at least in aged martensite, of cementite, which as a matter of fact would convert it into an aggregate. Lucas unhesitatingly states that martensite is an aggregate, and indeed, following Jeffries and others, we should regard martensite as made up of submicroscopic grains of ferrite with dispersed particles of cementite. Whether the alpha ferrite contains or not some carbon in solution appears to them to be relatively immaterial.

Formation of Martensite. — Passing now to the conditions necessary to form martensite it is evident from the answers received that metallurgists agree that in order to produce it and to retain it at room temperature, in iron-carbon alloys, the allotropic transformation of gamma iron must be delayed by sufficiently rapid cooling until a temperature of some 300 deg. C. is reached. In the presence of elements

such as nickel and manganese, sometimes referred to as retarding elements, less rapid cooling suffices. Indeed, slow cooling in air or even in the furnace of such alloy steels may cause the allotropic change to take place at 300 deg. C. and the steel to become martensitic. It is generally held that when austenite transforms at such low temperatures, the gamma to alpha allotropic transformation takes place, but for lack of the necessary plasticity the carbon or the carbide of iron is retained in solution in alpha iron although the latter has little if any dissolving power for carbon. This solid solution of carbon in alpha iron, therefore, is necessarily supersaturated, which, according to some, may account in part at least for its great hardness.

Why Martensite is Hard. — Whether a solid solution or an aggregate, we must seek the cause of the intense hardness of martensite. The following reasons have been given:

1. Because of the hardness of the carbon it contains;
2. Because of the hardness of the carbide it contains;
3. Because of the hardness of the iron it contains;
4. Because it is a solid solution;
5. Because it is a supersaturated solid solution;
6. Because of the distortion of the crystal lattices;
7. Because of the extreme fineness of its grain;
8. Because of the presence of numerous minute particles of the carbide Fe_3C, and
9. Because of internal strains.

Guillet, Jeffries, and Archer attribute the hardness chiefly to the smallness of the grains, Benedicks, Honda, and McCance chiefly to lattice distortions, Bain and Lester to both smallness of grain and lattice distortion, Thompson to lattice distortion and strains, Campbell and Lucas to the presence of carbide particles, Hatfield to the state of solution, and Stoughton to internal stresses within the crystals.

Positions Occupied by Carbon Atoms or Carbide Molecules. — Assuming with most, martensite, when freshly formed at least, to be a solid solution of carbon or of the carbide Fe_3C in alpha iron, let us inquire into the positions occupied by the carbon atoms or by the carbide molecules in the space lattices of the alpha crystals. A few only have answered that question, and it is evident that there is no substantial agreement among those who have devoted much time to the X-ray analysis of steel. To discuss their views here would be of little profit.

Influence of Strains. — The last question referred to the part played by strains in the hardening of steel. Here again opinions differ widely, some holding that strains play a very important part, some no part at all, while others believe that they may to a notable extent contribute to the hardness.

Conclusions. — The author believes that it is not possible to tell what is the prevailing view of metallurgists. Differences of opinion are met with at every stage, in regard to the condition of the carbon dissolved in gamma and in alpha iron, to the position occupied by the carbon atoms or by the carbide molecules in the crystal structure, to the nature of martensite and especially to its hardness, which is attributed to many causes.

The best that can be done is to state that it is generally, but not by any means universally, held (1) that freshly formed martensite is a solid solution of carbon or of the carbide Fe_3C in alpha iron; (2) that martensite forms, and is retained, when

austenite transforms in the vicinity of 300 deg. C.; (3) that on aging, minute particles of the carbide are thrown out of solution, converting the martensite into an aggregate; (4) that the hardness of martensite is due wholly or partly to one or more of the following causes:

(1) To its being a solid solution; (2) a supersaturated solid solution; (3) to the fineness of its grains; (4) to distorted space lattices; (5) to the presence of minute particles of the carbide, and (6) to internal strains.

It is also generally held that troostite is a very fine aggregate of ferrite and cementite.

It should be noted that, accepting these views of the nature of martensite and troostite, hardened steel frequently contains (1) undecomposed austenite, which is one phase; (2) martensite, another phase; and (3) troostite, a mixture of two phases, ferrite and cementite; that is, in all, four phases, which is not permissible in a system of two components. There must be something wrong with this conception.

Comparing the situation today with that of thirty years ago as presented in the author's first paper, the only progress (?) made towards a solution of the problem may be thus summarized: (1) Abandonment of the belief in the existence of beta iron; (2) X-ray analysis of iron-carbon alloys by which it is shown that gamma iron has a face-centered space lattice and alpha iron, as well as the iron present in martensite, a body-centered space lattice; and (3) the belief expressed by some that the hardness of martensite might be caused primarily (*a*) by the presence of extremely small (submicroscopic) ferrite grains, or (*b*) by the distortion of the space lattices resulting from the presence of carbon atoms in enforced solid solution. This does not constitute a very material advance, if advance at all, seeing that it has also introduced additional controversial matter.

Jeffries' and Archer's Slip Interference Theory. — In his answer to the questionnaire, Jeffries has summarized as follows the "Slip Interference Theory of the Hardening of Steel," which he and R. S. Archer have so ably presented:

1. I believe that freshly formed martensite in carbon containing steel is fine-grained ferrite, crystallizing with a body-centered space lattice, in which the carbon is largely atomically dispersed, and that the hardness is due principally to the grain refinement but partly to the carbon. In aged or tempered martensite the carbon may be partly or even largely associated to form myriads of minute particles of iron carbide partly within ferrite grains and partly at grain boundaries. The maximum hardness will probably occur at a certain stage of association of the carbon.

2. I believe the main condition necessary for the formation of martensite in carbon containing steel is the suppression of the transformation temperature of austenite by certain combinations of alloying elements and rates of cooling, to a temperature range within which the face-centered cubic space lattice of austenite can change to the body-centered cubic space lattice of ferrite independently of the iron carbide formation. While the mechanism of this change from austenite to martensite is very imperfectly understood, it seems probable that the transformation begins from many centers and the main change occurs by the progressive growth of the ferrite from these many centers. The austenite would of course decompose at the surfaces of ferrite grains. Only a slight shift in the atoms is required to produce this change. The carbon would be largely trapped in substantially the same distribution in which it existed in the austenite. The carbon atoms can diffuse slowly at room temperature and more rapidly at higher temperatures. A small amount of iron carbide could form simultaneously with the austenite transformation. The rate of diffusion of the carbon is so slow that the carbide formation is not completed except after very long aging at room temperature, the time becoming shorter the higher the temperature.

3. I believe that such carbon as remains in atomic dispersion in the ferrite is probably in between the space lattice points. I do not believe that Fe_3C is in solid solution in the ferrite.

4. I believe internal strains play an important part in the *hardening* of steel chiefly because of

the volume changes accompanying the transformations; i.e. strains determine in part to what extent the main transformation takes place. I do not believe that internal strains have any important direct bearing on the *hardness* of steel. If there is any effect, internal strains would probably decrease rather than increase hardness.

Referring to the descriptive title selected by Jeffries and Archer for their theory, the author believes that any hardening theory may be described as a slip interference theory on the ground (1) that hardness means resistance to plastic deformation, (2) that deformation in metals occurs through crystalline slips, and (3) that increased hardness therefore, regardless of its cause, necessarily implies greater resistance to slip, that is greater slip interference.

Hanemann's and Schrader's Theory. — Dr. H. Hanemann and Miss A. Schrader present an entirely new explanation of the nature of martensite and of the hardening of steel, involving the formation in quenching of two new phases, *epsilon* and *eta* in metastable equilibrium with austenite. (Tran. Am. Soc. for Steel Treating, February, 1926.) It is not discussed in these pages because of its newness and highly speculative character, it being the author's desire to include in the kind of treatise he is writing only theories and hypotheses reasonably supported by experimental evidence and which have successfully passed the gauntlet of justified criticism. Dr. Hoyt supports this explanation, as will be seen from his answers to the questionnaire when he writes:

1. My opinion of the nature of martensite is practically as given in the Hanemann-Schrader paper of 1925. The hardness is due to the phase of about 0.9 per cent carbon in which the carbon and iron are in forced solution or combination. The high mineralogical hardness would be due to the new interatomic bonds which are thereby set up.

2. Martensite forms when austenite is quenched sufficiently rapidly to retain the gamma iron solid solution down to about 300 to 350 deg. C. At that temperature austenite changes to what we call martensite. The mechanism is about as given by Hanemann and Schrader.

3. After calculating the number of atoms of carbon which may replace the iron atoms in the body-centered cubic lattice, and given the density and lattice parameter, as measured, my opinion is that a 0.9 per cent carbon martensite has about half its carbon atoms in the lattice and the other half of its carbon atoms in the interstices. No cause for such an atomic arrangement is known to me and it may be found later, contrary to this picture, that the distribution is simple.

4. Due to the fact that hardening involves an appreciable volume change, I believe that strains must play an important rôle in the process through the pressure effects which they will set up. If the pressure distribution were known, the effect would be that predicted by applying the principle of Le Chatelier.

Answer of the Author to the Questionnaire. — In answering his own questionnaire and in briefly expressing his views in regard to the hardening of steel, the author does not claim in any way to have solved the problem discussed in this chapter. He feels today exactly as he did thirty years ago, when, after outlining some conception of the possible cause of hardening, he wrote, in concluding his paper: "The writer does not wish to advance here any new theory. Indeed, if he knew that his remarks would be so interpreted he would refain from giving them shape. He only feels that they may contain some element of truth which may help in solving the problem discussed in this paper, and if his arguments and deductions are not sound, he hopes they will be promptly refuted."

Fortunately, he is not wedded to any theory. He is ready to abandon any he may at one time have defended for any other which may appear more logical or more useful. Theories are tools, and we should use the best tools obtainable.

The views to be presented here, tentatively and cautiously, appear to be in better agreement with observed facts and experimental evidence as well as with the phase

rule, which at least they do not violate. They are based largely on the microstructure of "martensite" needles under very high magnification as brought out by Lucas, on the behavior of austenite on tempering, and on the behavior of troostite. They will be concisely expressed.

Austenite is a solid solution of the carbide Fe_3C in gamma iron.

Troostite is a solid solution of the carbide Fe_3C in an allotropic form of iron different from the gamma form and which for the present will be designated as non-gamma iron. The fact that the resolution of troostite fails to reveal the network structure generally found in solid solutions may be ascribed to the grains being sub-

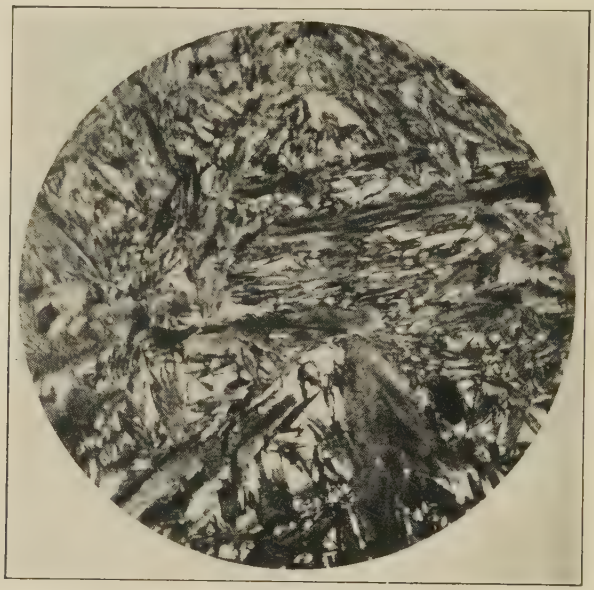


Fig. 215. — Steel 1 to 1.1 per cent carbon; quenched from a high temperature; etched with picric acid. Original magnification 3230 diam. (F. F. Lucas.)

Rod was heated at one end to a high temperature and quenched. This field is well toward hard end of specimen and shows very early stages of troostitic development along martensitic needles and as nodules (two of which are seen). Troostite is quite dark, martensite much lighter, austenite white.

microscopic, which in turn may explain, partly at least, the hardness of troostite. Lucas finds that what he calls nodular troostite contains radial grains which, under the highest powers of the microscope, exhibit all of the characteristics of solid solutions. When undecomposed, he reports that these grains consist of a single constituent, and that they display orientation phenomena when revolved about the optical axis of the microscope.

Austenite always transforms into troostite on slow or rapid cooling, as well as in tempering after quenching.

In his paper of 1896, the author wrote:

"While we know with reasonable certainty the composition of ferrite, cementite, and pearlite, we know very little about the true nature of martensite. Indeed, if we could discover its composition, the hardening of steel would no longer be an un-

solved problem. Each theory which has been advanced to explain the hardening of steel has attributed to martensite the composition demanded by that theory. Of its real composition, however, we have no direct evidence. Unfortunately, the details of its structure are so minute and so difficult to resolve that, even when most highly magnified, it gives little indication of its chemical composition or even structural character."

The remarkable high-power photomicrographs recently obtained by Mr. Lucas have supplied what we were so much in need of thirty years ago and have confirmed my belief in the duplex nature of this so-called martensite.

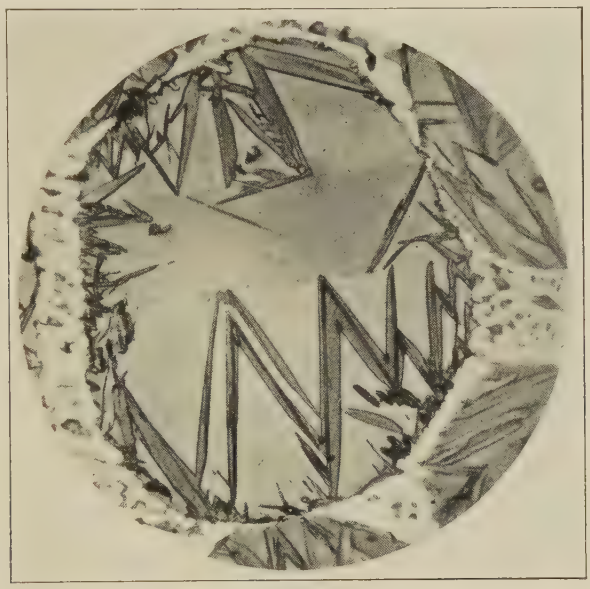


Fig. 216. — Iron-carbon alloy; 2.65 per cent carbon; quenched in iced brine from 1260 deg.C.; etched 3 min. in picric acid. Original magnification 2450 diam. (F. F. Lucas.)

The structure of hardened steel containing from 1.00 to 1.10 per cent carbon is seen under an original magnification of 3230 diameters in Figure 215. It is customary to state that the dark needle-like constituent is martensite, itself a solid solution of carbon in alpha iron, and the lighter one, undecomposed austenite. In that light, hardened steel must be considered as an aggregate of austenite and martensite. On close examination, however, we note that the steel also contains particles decidedly darker than the so-called martensite needles, and we call these particles troostite, which we describe as an aggregate of finely divided ferrite and cementite. Hence, as already mentioned, the presence of four phases.

Lucas writes: "No evidence has been found that a plain carbon steel may become fully martensitic. The structures at high power are seen to consist of austenite and martensite, but more often of austenite, martensite, and troostite, sometimes of even lower orders of decomposition."

In order to study the nature of martensite we may confine our attention to a few needles as they appear under very high magnification, (1) in quenched samples and

(2) after prolonged tempering. Martensite needles embedded in an austenite matrix are seen in Figures 216 and 217, representing the structure of an iron-carbon alloy containing 2.65 per cent carbon and quenched in iced brine from a temperature of 1260 deg. C. The original magnifications were, respectively, 2450 and 2100 diameters. The conditions are here at their best to study the structure of the needles and the transformation of both the needles and the austenitic matrix on tempering.

We find that the needles themselves are not made up of a single phase but clearly of two phases — that they are therefore of the nature of an aggregate. They all have a central or mid rib which is much darker than the surrounding metal. I believe this

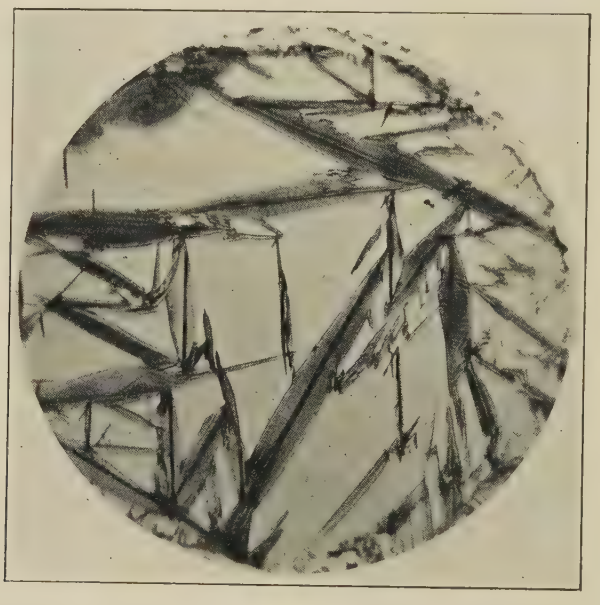


Fig. 217. — Same as Figure 216; another spot; 1260 deg. C., quenched in brine. Original magnification 2100 diameters.

midrib to be made up of troostite, a solid solution of carbon in non-gamma iron resulting from the allotropic transformation of austenite along its octahedral cleavage planes. I believe the balance of the needles to consist of austenite in which troostite is present too finely divided to be detected even under very high magnification but in sufficient quantity to result in a darker coloration of the needles by etching compared to the color of the undecomposed austenite surrounding it. This transformation of austenite into troostite through the formation of troostite-austenite needles (martensite) along the octahedral cleavage planes of austenite is well illustrated by Lucas in Figure 218.

These views demand that in tempering, austenite should transform into troostite (a solution of carbon in non-gamma iron), and this, I believe, is precisely what happens, as revealed by some experiments [1] conducted by Lucas. This long tempering of a quenched high carbon steel consisting of martensite needles in an austenite matrix did not result in the formation of additional needles but clearly in additional troostite

[1] The sample which after quenching had the structure shown in Figures 216 and 217 was tempered by him for thirteen hours at 200 deg. C., repolished, re-etched, and again photographed, as shown in Figures 219 and 220, under an original magnification of 3500 diameters.

causing the original needles to color darker and in the occurrence of many troostitic fringes around the needles and of troostitic particles in the austenitic matrix.

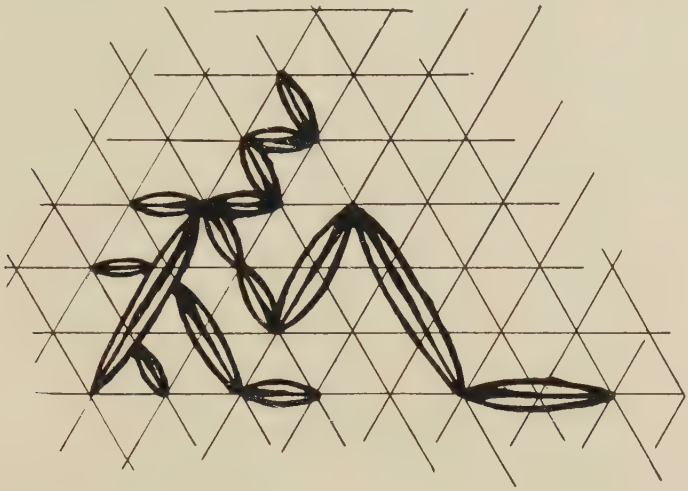


Fig. 218. — Development of martensite along cleavage planes parallel to surface of an octahedron. Three sets of planes. (F. F. Lucas.)

Fig. 219. — Same sample as illustrated in Figures 216 and 217. Brine-quenched from 1260 deg. C.; tempered 13 hours, 20 min., at 200 deg. C.; etched 10 sec. in picric acid. Original magnification 3500 diam. (F. F. Lucas.)

It should also be noted that while it required three minutes in picric acid to bring out the structure of the sample as quenched, ten seconds sufficed after the sample had been tempered, a strong evidence of the presence of much more troostite in the latter.

Condition of Iron in Troostite. — Passing now to the important question of the condition of iron in troostite, which I have so far described as non-gamma, our first impulse must be to infer that it is alpha iron. Alpha iron, however, has little if any dissolving power for carbon, from which it follows that carbide should always be rejected from troostite both on slow cooling and on tempering. Lucas, however, finds that while carbide is expelled from troostite of hyper-eutectoid composition, ferrite is expelled from hypo-eutectoid troostite, clearly indicating that the iron in troostite is capable of dissolving carbon up to the eutectoid point.

Troostite, in this light, must be considered as a solution supersaturated with carbide when it contains more than 0.85 per cent carbon. Were it not for the ire it

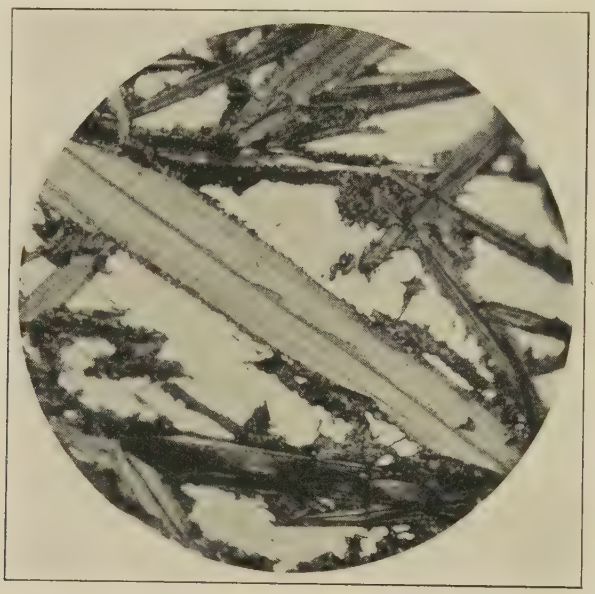


Fig. 220. — Same as Figure 219; another spot.

would arouse in some, I should be tempted to call this non-gamma iron capable of dissolving carbon, beta iron, although fully realizing that this beta iron may yield an X-ray spectrum similar to that of alpha iron and of delta iron.

This conception of the nature of austenite, troostite, and martensite leads us to visualize the transformation of austenite into pearlite as follows:

The complete transformation of austenite into pearlite requires time and plasticity, hence slow cooling from a sufficiently high temperature. Assuming, for the sake of simplicity, the steel to be of eutectoid composition, when it enters its critical range, austenite begins to transform allotropically into a solid solution of carbon in non-gamma (beta?) iron, which, in my opinion, is troostite. Time is required for the complete transformation of austenite into troostite, and finely divided aggregates of austenite and troostite are necessarily formed which hitherto have been called martensite and have generally been considered as solid solutions. The austenite-troostite transformation begins along the octahedral cleavage planes of austenite, giving rise to the well-known so-called martensite needles. These needles consist of a midrib of solid troostite surrounded by austenite holding very finely divided particles of troostite. Further transformation results in the growth of the needles at the expense of the untransformed

austenite and in the final complete transformation of austenite into troostite. The next step in the transformation consists in the formation of alpha iron, and simulta-

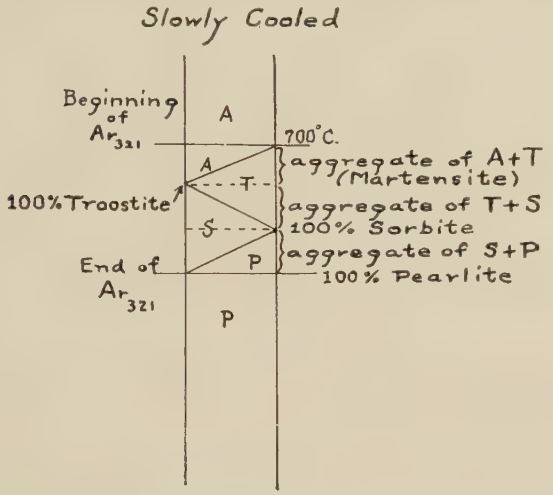


Fig. 221. — Diagram showing transformation of austenite into pearlite.

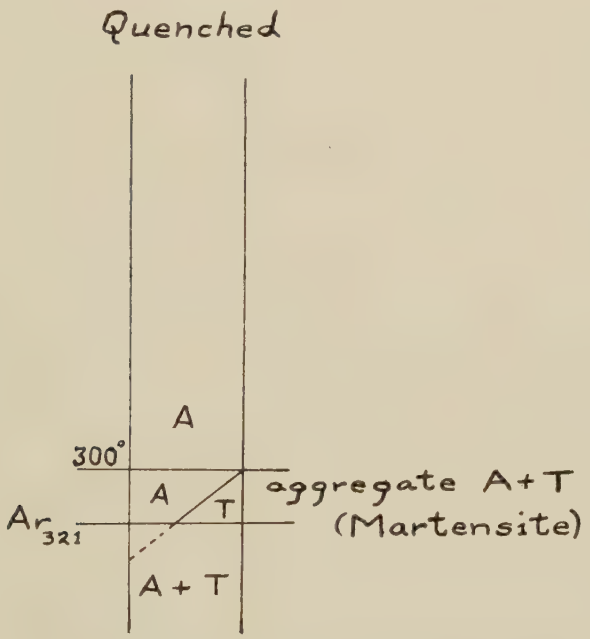


Fig. 222. — Diagram showing transformation in cooling austenite so that the austenite-troostite aggregate is retained and the steel is hardened.

neously, since alpha iron cannot dissolve carbon, in the rejection of carbide, resulting in the formation of sorbite. This is followed by the coagulation of the cementite particles into plates, resulting in the production of pearlite. In cooling austenite at

such a rate that its transformation is delayed until a temperature of some 300 deg. C. is reached, the austenite-troostite aggregate is retained and the steel is hardened. These views are expressed diagramatically in Figures 221 and 222.

Summary. — Austenite is a solid solution of carbon, probably in the form of the carbide Fe_3C in gamma iron.

Troostite is a solid solution of iron and carbon, probably in the form of the carbide Fe_3C in non-gamma iron.

Austenite always transforms into troostite regardless of the temperature at which the transformation takes place.

Martensite is the aggregate of austenite and troostite necessarily resulting from the *gradual* transformation of austenite into troostite.

Troostite of eutectoid composition transforms into sorbite.

Troostite of hypo-eutectoid composition transforms into sorbite after rejection of the "excess" ferrite.

Troostite of hyper-eutectoid composition transforms into sorbite after rejection of the "excess" cementite.

The rejection of some cementite from hyper-eutectoid troostite and of ferrite from hypo-eutectoid troostite may take place at room temperature, from which it follows that aged troostite may be described as an aggregate consisting of minute particles of the carbide Fe_3C or of ferrite in a matrix of the solid solution of the carbide in non-gramma iron, that is of true troostite.

The transformation of troostite into sorbite implies an allotropic transformation and the formation of a very fine aggregate of alpha ferrite and of cementite.

Pearlite results from the coagulation into plates of the constituents of sorbite.

Gamma iron being unstable at room temperature, austenite, on reheating, tempers into troostite through the allotropic transformation of gamma iron and the retention of the carbide in solid solution.

Troostite, on further reheating, tempers into sorbite through the formation of alpha iron and the rejection of cementite.

Austenite is harder than gamma iron because it is a solid solution, it being well known that solid solutions are generally harder than the solvent.

Troostite is harder than austenite, possibly because the iron it contains is harder than alpha iron; also possibly because of the presence in troostite of submicroscopic grains offering greater resistance to slip, the structure of troostite being much finer than that of austenite; because of the distortion of its crystal lattice, or, again, because of the existence of severe internal strains.

The hardness of troostite increases with the percentage of carbon it contains, possibly because of increasingly smaller grains.

The aggregate martensite is harder than the troostite it contains and *a fortiori* harder than the austenite because the structural arrangement of these two constituents offers greater resistance to slip than plain troostite. Its very acicular structure favors that view, as pointed out by Thompson, who writes, " . . . the needles formed act as strengthening scaffolds throughout the mass."

The hardness of martensite increases with its carbon content because of the greater hardness of the troostite it contains, and possibly also because finer needles and finer grains result from the transformation of austenite containing much carbon.

We are naturally led to inquire into the proportions of austenite and of troostite which should be present in the aggregate martensite in order to obtain maximum

hardness for a given percentage of carbon. The answer may be that we should have as many needles as possible on the ground that the greater the number of needles the greater the slip interference. This would be in line with the increased hardness resulting from an increasing percentage of carbon because as the carbon increases the needles become smaller and hence more numerous.

It is well to bear in mind that although the author has arrived independently at the views he has tried to express in regard to the nature of hardened steel, he is not the first who has considered martensite to be an aggregate and not a solid solution, as is apparent from the views expressed by eminent metallurgists. Those, however, with the exception of Lucas, who have referred to martensite as being an aggregate, also describe troostite as an aggregate. Lucas believes troostite to be a solid solution and martensite an aggregate of ferrite and cementite, while the author considers martensite to be an aggregate of austenite and troostite. Dejean has indicated the possibility of two solid solutions being present in martensite, one of carbon in gamma iron and the other of carbon in alpha iron, but there is no evidence that he identifies the latter with troostite. Boylston, however, refers to the possible presence of troostite in so-called martensite needles.

Hardness of Solid Solutions. — Since in final analysis most metallurgists believe that the hardness of quenched steel is due, at least largely, to its containing a solid solution, it seems advisable to consider briefly the reasons that have been advanced to explain the hardness of solid solutions both immediately after their formation as well as the increased hardness frequently observed on aging or after slight reheating.

The greater hardness of solid solutions compared to that of the solvent has been ascribed (1) to a greater attraction between unlike atoms, (2) to smaller grains, and (3) to distortions of the space lattice of the solvent caused by the presence of foreign atoms, while the increase of hardness resulting from aging, or slight heating, is generally ascribed to the coming out of solution of some of the solute in the form of extremely minute particles, the particles themselves being harder than the solvent. The solute may be, and frequently is, a metallic compound. Maximum hardness corresponds to a degree of dispersion of the solute called the critical dispersion. Past that point further precipitation of the solute causes it to occur in larger-sized particles, and the hardness begins to diminish. The greater hardness resulting from precipitation and dispersion of minute particles of the solute is explained by Jeffries and others as due to increased resistance to slip resulting from the "key action" of these particles.

According to Honda the hardness of solid solutions is maximum when it contains equal atomic proportions of the components.

In order to clarify, let us apply these views to the aluminum-copper alloys known as duralumin, and which generally contain not over 4 per cent copper. At a high temperature solid solutions are formed, which can be retained at room temperature by quenching but which when thus retained are in a supersaturated and hence metastable condition. The alloys are then considerably harder and stronger than the solvent aluminum. On aging the hardness is further increased through the separation of many and very small particles of the compound $CuAl_2$. Maximum hardness is generally obtained after a period of four days, although no change in the microstructure is observable, this being ascribed to the submicroscopic size of the particles of $CuAl_2$.

The general conclusion is thus reached that hardening resulting from quenching followed by aging is always due to the preservation at room temperature of a supersaturated, metastable solid solution, followed, on aging or slight reheating, by a pre-

cipitation of some of the solute (frequently a metallic compound) in an extremely fine state of division.

Applied to the hardening, by quenching, of iron-carbon alloys, the theory demands the retention at room temperature of a solid solution, namely carbon or the carbide Fe_3C in alpha (or beta?) iron, and the subsequent precipitation of minute particles of Fe_3C. In the present instance, however, the solid solution thus retained by quenching is so unstable that little if any aging is required to cause the precipitation of the carbide particles, which may take place simultaneously with the formation of that solution.

The hardening of iron-carbon alloys by quenching differs, however, in a very marked degree, from the hardening of other alloys by such treatment, because the solvent iron undergoes in the quenching bath an important allotropic transformation. While before quenching it consists of a solid solution of carbon in gamma iron (austenite), after quenching it is generally believed to be a solid solution of carbon in alpha iron. Admitting this, and admitting that alpha iron has little if any dissolving power for carbon, the resulting solution must be more severely supersaturated and metastable than if a solution in gamma iron had merely been retained, hence possibly the much greater hardness resulting from quenching iron-carbon alloys compared to the increased hardness of other alloys after quenching, and hence also, possibly the relatively unimportant action of aging. Were it possible to retain at room temperature the solid solution austenite existing at a high temperature, we would find that the hardness is considerably greater than that of the solvent iron. Austenite, judging from the hardness of alloy austenitic steel (manganese and nickel steels), probably has a Brinell hardness of about 225 while that of iron does not exceed 90. The hardness of martensite, however, is in the vicinity of 600, and we naturally ask why a solid solution of carbon in very soft alpha iron is so very much harder than a solution of the same amount of carbon in gamma iron. To seek an answer to that question would cause us to reopen the discussion of the hardening of steel already considered at some length in this chapter.

According to Jeffries and Archer, this much greater hardness of martensite is due primarily to the submicroscopic size of the ferrite grains. Were it possible to obtain these submicroscopic grains in the complete absence of carbon, the hardness would not be greatly less and possibly also submicroscopic grains of gamma iron would be equally hard. Others, as already noted, would attribute this great hardness to the presence of distorted lattices. Again it should be remembered that some still believe that the strains resulting from quenching because of the transformation with *increased* volume of gamma into alpha iron may be the chief cause of the hardness. Such strains have been claimed to produce numerous twins and hard amorphous layers.

Part Played by Carbon in the Hardening of Steel. — Any acceptable theory must explain satisfactorily the part played by carbon in hardening steel, that is, it must account for the much greater hardness after quenching of high carbon steel. Jeffries and Archer explain that the presence of sufficient carbon in the steel causes the austenite to transform at about 300 deg. C. if the speed of cooling is sufficiently fast, and that when the transformation occurs at that temperature, submicroscopic crystals of alpha iron are formed and the steel fully hardened. With less carbon, assuming the same cooling velocity, the transformation occurs at a higher temperature, resulting in larger alpha crystals, hence in less hardness. In the complete or nearly complete absence of carbon it is not possible, according to these authors, no matter how fast

the cooling, to depress the transformation to a temperature sufficiently low to cause the formation of small alpha crystals; austenite transforms at a relatively high temperature, large alpha crystals are formed, and the metal remains soft, hence the impossibility of materially increasing by quenching the hardness of carbonless or nearly carbonless iron. Were it possible, however, to cause the transformation of pure iron to occur at 300 deg. C. it should be nearly as hard as quenched carbon steel because it would consist of alpha crystals of submicroscopic size. Those who believe that hardness results from the distortion of the crystal lattices by carbon atoms must contend, it would seem, that the greater hardness of high carbon steel is due to a greater distortion of the lattices, since the complete or nearly complete absence of carbon must result in little or no distortion.

The advocates of the allotropic theory of the hardening of steel claimed that the carbon acted as a brake in preventing the transformation of hard beta iron into soft alpha iron, and that the more carbon present the more powerful was the brake, hence the harder the quenched metal.

CHAPTER XVII

MISCELLANEOUS HEAT TREATMENTS

There are some heat treatments which cannot be classified under any of the terms generally employed. They will be considered in this chapter.

Crystalline Growth of Ferrite Below the Critical Range. — Stead in 1898 showed that *strained* ferrite, when heated close to but below the critical range of the metal, undergoes a marked crystalline growth caused by adjoining ferrite grains assuming the same crystalline orientation and therefore merging into larger grains. It seemed

Fig. 223. — Steel. Carbon 0.05 per cent. Magnified 6 diameters. Subjected to Brinell ball test under pressure of 6000 kilograms and heated to 650 deg. C. for seven hours. Vertical section through bottom of spherical depression. (J. O. Connolly, in the author's laboratory.)

evident from Stead's experiments that unless the ferrite be strained (through cold working or otherwise) it will not grow on annealing, and also that the presence of a relatively small amount of carbon (some 0.15 per cent or more) effectively prevents the growth of the ferrite grains, apparently because of the pearlite particles standing in their way and preventing their merging. The author conducted in his laboratory some experiments, the results of which have thrown additional light upon this crystalline growth.[1]

The following extracts from a paper by the author presented at the sixth Con-

[1] These experiments were made by J. O. Connolly, at the time a research student at Harvard University.

gress of the International Association for Testing Materials describe briefly some of the most significant results obtained.

In Figure 223 is shown the slightly magnified structure of a steel containing 0.05 per cent carbon which had been subjected to the Brinell ball test [1] under a pressure of 6000 kilograms and then annealed at 650 deg. C. for seven hours. The section shown is a vertical one passing through the bottom of the spherical depression made by the 10-mm. ball used. It will be obvious that the strain was most severe at *A*, that is at the very bottom of the depression, and that it decreased gradually in intensity from *A* to *D*. The following features of the structure should be noted as having

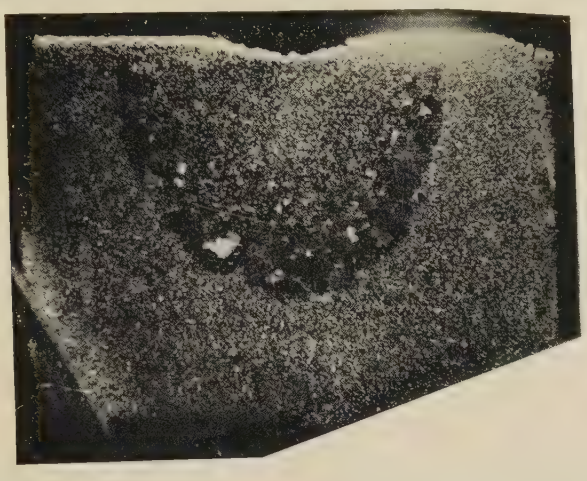


Fig. 224. — Steel. Carbon 0.05 per cent. Magnified 6 diameters. Subjected to Brinell ball test under pressure of 3000 kilograms and heated to 650 deg. C. for seven hours. Vertical section through bottom of spherical depression. (J. O. Connolly, in the author's laboratory.)

special significance: (1) At *D* where the metal was but slightly if at all strained no crystalline growth occurred, (2) at *C* where the strain must have been more severe a sudden growth of maximum intensity has taken place, (3) from *C* to *B* as the severity of the strain increases the crystalline growth shows a gradual *decrease*, and (4) from *B* to *A*, that is with further increase of the intensity of the strain, no crystalline growth has taken place. These observations point to the conclusion that ferrite grains will not grow on annealing below the critical range unless they have been subjected to a certain stress creating a certain strain, and that they will not grow if that stress, and therefore the resulting strain, has been exceeded. In other words, they point to the existence of a critical strain producing growth, strains of greater or less magnitude being ineffective. The narrow region occupied by the critically strained metal should also be noted, as well as the very sharp line of demarcation between the critically strained and the understrained metal. The separation of the critically strained metal from the overstrained is not so sharp.

Similar experiments were repeated many times and like results always obtained.

[1] In using the Brinell ball test as a suitable means of straining ferrite in order to study its growth on annealing the author followed Charpy.

A piece of the same steel was subjected to exactly the same treatment, except that the ball pressure applied was 3000 kilograms or half the pressure applied to the pre-

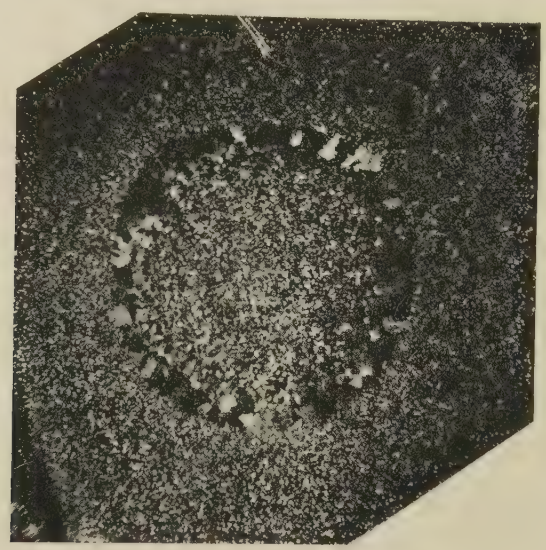


Fig. 225. — Steel. Carbon 0.05 per cent. Magnified 6 diameters. Subjected to Brinell ball test under pressure of 3000 kilograms and heated to 650 deg. C. for seven hours. Horizontal section through bottom of spherical depression. (J. O. Connolly, in the author's laboratory.)

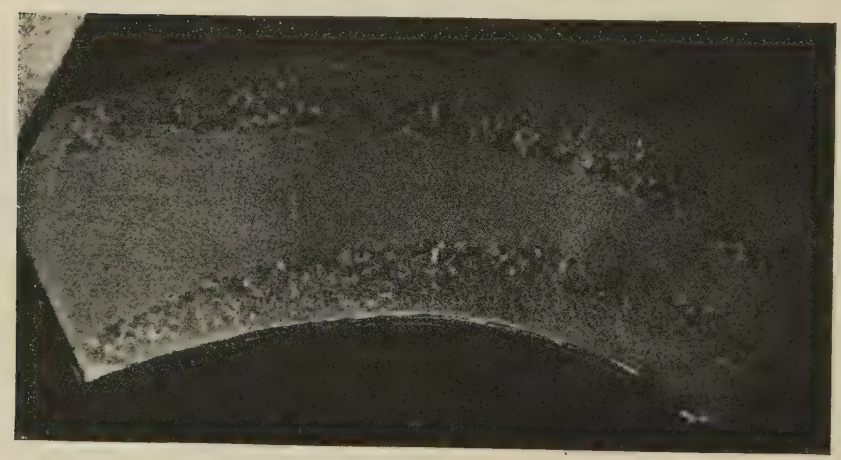


Fig. 226. — Steel. Carbon 0.05 per cent. Magnified 3 diameters. Bar bent double and heated to 650 deg. C. for seven hours. Longitudinal section through center of bent portion. (J. O. Connolly, in the author's laboratory.)

vious one. The crystalline growth resulting from the annealing of this sample is shown in Figure 224. Because of the smaller stress applied, the critically strained portion of the metal is nearer the depression. This would naturally be expected. Here, as in the previous case, we have three distinct regions: (1) the metal surrounding

the depression and extending to a certain distance which was too severely strained to grow, (2) the critically strained metal in the form of a spherical shell, and (3) the rest of the metal unstrained or too feebly strained for the growth to take place.

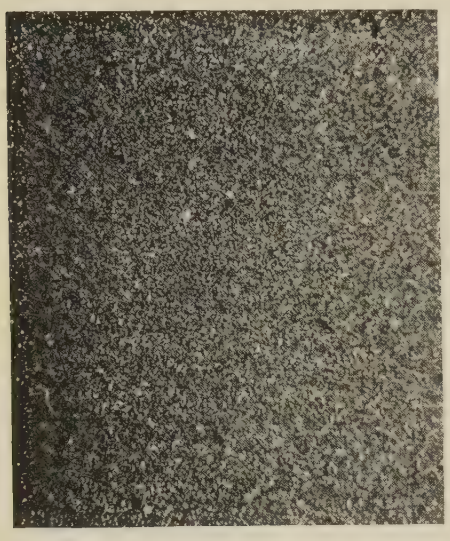


Fig. 227. — Tensile stress, 38,000 lbs. per sq. in.

Fig. 228. — Tensile stress, 42,000 lbs. per sq. in.

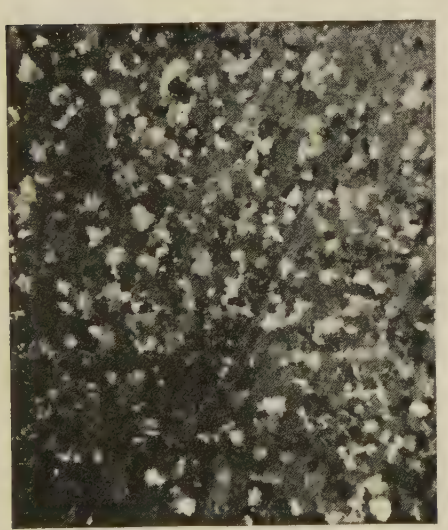


Fig. 229. — Tensile stress, 40,000 lbs. per sq. in.

Fig. 230. — Tensile stress, 44,000 lbs. per sq. in.

Figure 225 is a section through a similar sample, the specimen having been ground level with the bottom of the depression. The occurrence in this section of a ring showing crystalline growth will be readily understood.

In Figure 226 is shown the structure of a bar of the same steel which after having been bent was subjected to annealing (seven hours at 650 deg. C.). A piece of the

bent portion of this bar was then cut and a longitudinal section through its center prepared for microscopical examination. It will be obvious that the upper part of the bent portion of the bar was subjected to severe tension and the under part to severe compression. Somewhere between the upper and lower parts a neutral plane existed which was subjected neither to tension nor to compression, and in the vicinity of this plane the metal was but slightly strained. Moving in both directions from this neutral plane, the metal becomes gradually more severely strained. Figure 226 shows that (1) in the center of the bar no growth took place, the metal being here understrained; (2) as soon as the critically strained portion was reached a very abrupt growth occurred of maximum intensity, and (3) this growth decreased gradually as the metal became more severely strained, being very slight if existing at all where the strain was maximum, that is near the upper and under parts of the bend. The widening of the central zone, free from growth as the distance from the bend increases, is also consistent with the existence of a critical strain, for it is evident that the portion of unstrained or understrained metal increases with that distance. Incidentally this experiment shows that tension is apparently as effective as compression in producing crystalline growth, there being apparently no difference in the size of the ferrite grains between the upper and under parts of the bar. The critically strained portions occupy also nearly the same position with regard to the outside surfaces, that is, they occur at the same depth. Their width also appears to be the same.

Bars of the same steel were subjected to compression, shearing, and twisting stresses and the results obtained were in every case consistent with the existence of a critical strain.

With a view of securing some data in regard to the magnitude of the critical stress needed to induce growth on annealing, a number of bars of the same steel were subjected to tensile stresses of increasing intensity, annealed at 650 deg. seven hours, and in every case a cross section of the strained and annealed bar was prepared for microscopical examination. The elastic limit or rather yield point of the metals was in the vicinity of 28,000 lbs. per square inch, and its ultimate strength 45,600 lbs. per square inch.

In Figures 227 to 230 are shown the structures of the bars subjected respectively to stresses of 38,000, 40,000, 42,000, and 44,000 lbs. per square inch.

These tensile tests afford another conclusive evidence of the existence of a critical strain and the fact that a stress of 40,000 lbs. per square inch produces a marked growth, while stresses but slightly inferior or superior, namely 38,000 and 42,000 lbs. per square inch, do not induce growth, is an indication of the narrowness of the range of the critical stress.

A striking illustration of the existence of critically strained metal is shown in Figure 231 after C. Chappell, in the form of longitudinal sections through broken tensile test pieces heated for two hours at 600 deg. C. Here again the demarcation between the understrained portion and the critically strained one is sharper then between the latter and the overstrained portion.

The contention of some that if time be given the overstrained portion also will grow does not remove the gap existing between critically strained metal responding so readily to the annealing treatment and overstrained metal, if not absolutely recalcitrant, at least extremely refractory to the treatment.

In subjecting electrolytic iron of great purity to the treatments producing the crystalline growth of ferrite described above, Stead reports that he was unable to

cause its grain to grow. The author likewise has never succeeded in producing a growth, at least in any appreciable degree, in wrought iron or in practically carbonless iron such as American ingot iron. It seems certain that a small amount of carbon, preferably in the vicinity of 0.05 per cent, must be present. On the other hand he has never succeeded in coarsening appreciably, by similar treatments, the grain of steel containing over 0.12 per cent carbon. It would seem, therefore, that we must also recognize the existence of a critical carbon content (0.04 to 0.12 per cent) above or below which ferrite grains will not grow on annealing below the range, even if they have been critically strained.

From what has been said of the crystalline growth of strained ferrite under its critical range, and considering that cold drawn steel wires are frequently annealed

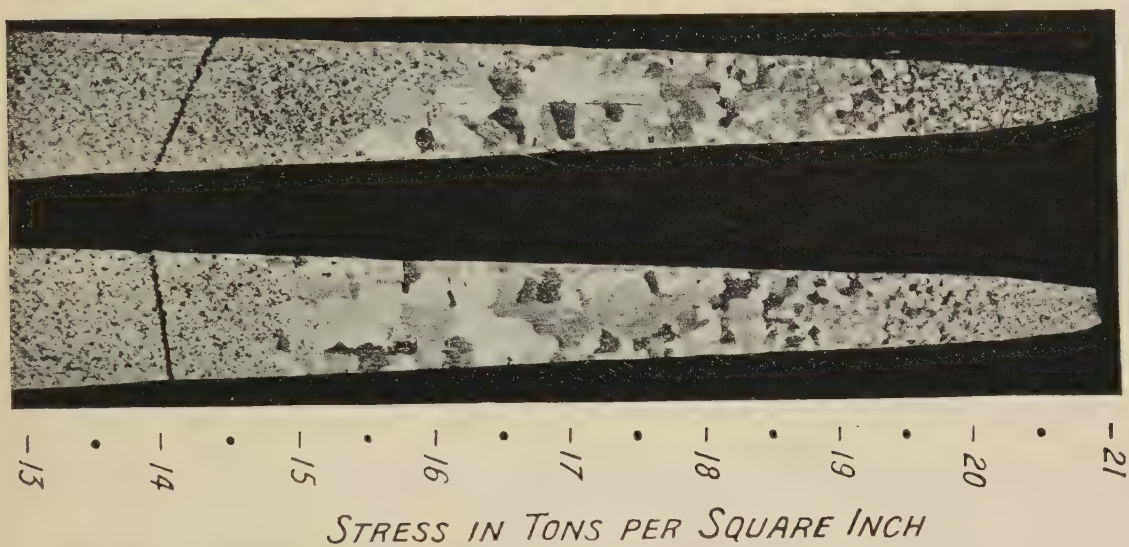


Fig. 231. — Longitudinal sections through broken tensile test bars heated for 2 hours at 600 deg. C. Magnified 4.75 diameters. (C. Chappell.)

at such temperature, it may reasonably be asked why they are not rendered thereby coarsely crystalline and brittle. Obviously because steel wires when subjected to the annealing treatment are generally in a decidedly overstrained condition. If very low carbon steel wire be given a draft so light that it is critically strained, heating it for a sufficient length of time at some 600 deg. C. will cause the crystalline growth of ferrite, as should be expected. In such critically strained metal, however, the growth may be prevented by heating to a decidedly lower temperature, as for instance to 525 or 550 deg. C., which is sufficient to remove materially the brittleness resulting from cold working or, of course, by annealing above the critical range.

According to Kenneth B. Lewis, in wire drawing the reduction should not be less than 20 per cent in order to avoid the production of critically strained metal and hence dangerous crystalline growth on subsequent annealing below the thermal critical range.

Robin believes that the straining of ferrite results in the creation of a number of nuclei (*germes*) from which new grains will grow on annealing. To account for the existence of a critical strain it might be argued (1) that in understrained metal these

nuclei are not formed, (2) that in critically strained metals a few nuclei are produced giving rise on annealing to a few large grains, and (3) that in overstrained metal a great many nuclei form, producing on annealing a great many and therefore, necessarily, smaller grains.

Beilby's amorphous theory briefly explained in Chapter I seems to afford the most acceptable explanation of the crystalline growth of strained ferrite below its critical range, on the ground that the amorphous iron produced by straining, re-

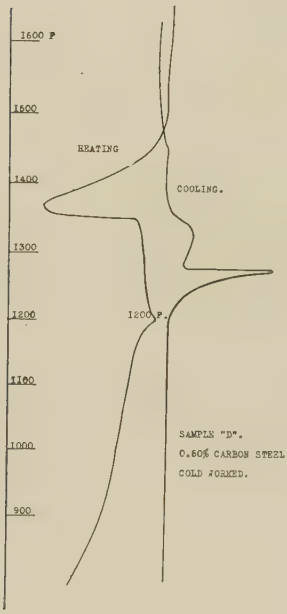


Fig. 232.

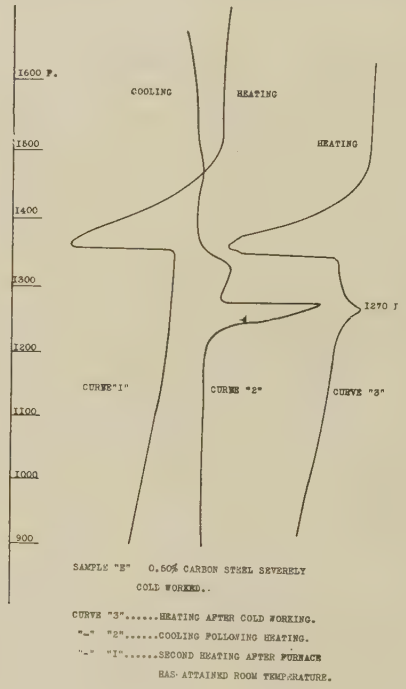


Fig. 233.

crystallizes below the range. Howe has suggested the following ingenious hypothesis to account for the existence of a critical strain: (1) the crystalline growth of ferrite is an electrolytic process in which the amorphous iron acts as electrolyte; (2) if the iron be overstrained the quantity of amorphous iron is so great, that is there is so much electrolyte, that electrolysis can take place across it only very slowly, hence the slowness or entire absence of crystalline growth; (3) in understrained iron there is no growth because of the presence of an insufficient amount of amorphous iron, that is of electrolyte, and (4) in critically strained metal the proportion of amorphous iron is such as to lead to rapid electrolysis, that is to rapid growth. "In short," Howe writes, "the very rapid coarsening implies the presence of enough electrolyte to give electrolysis a chance, yet not so much electrolyte as to cause too great a barrier to electrolysis by its width. Again, if the quantity of the electrolyte was excessive that would mean that the quantity of crystalline iron remaining was small. Now it is only the crystalline iron which can form grains and hence can coarsen, and if this iron is reduced to too small a quantity it might readily follow that the residual crystalline iron was not abundant enough to form large grains."

Further investigation of the growth of strained ferrite on annealing has shown, as already noted in Chapter I, that the more severe the strain, the lower the tempera-

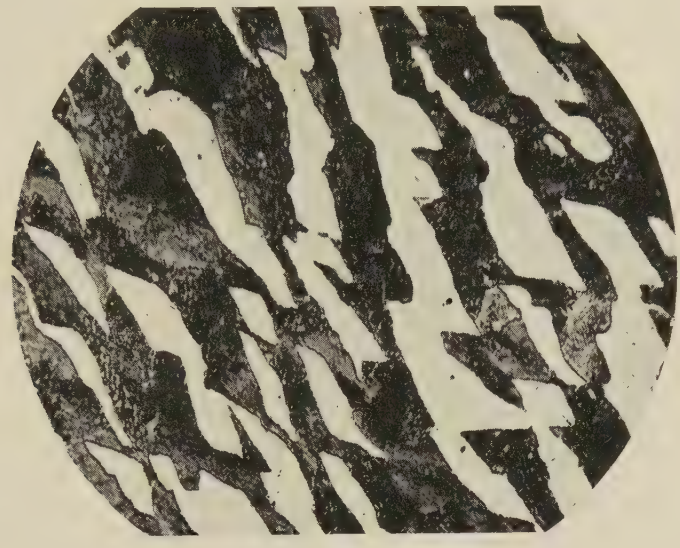


Fig. 234. — Cast steel. 0.50 per cent carbon. Cold worked and reheated below the A_x point. Magnified 350 diameters. (V. N. Krivobok.)

Fig. 235. — Cast steel. 0.50 per cent carbon. Cold worked and reheated above the A_x point. Magnified 350 diameters. (V. N. Krivobok.)

ture at which large grains are formed, from which it may be inferred that to each degree of strain corresponds also a critical grain growth temperature. This temperature has been called "germinative temperature" by Howe. It is also true that the

higher the germinative temperature, the larger will be the grain, from which it follows that in slightly strained metals larger grains will form at their germinative temperatures than in severely strained metals at their germinative temperatures.

Heat Evolution vs. Recrystallization. — Dr. V. N. Krivobok has found that when samples of hypo-eutectoid steel and of armco iron are cold worked and then heated, an evolution of heat is observed in the vicinity of 650 deg. C. (Fig. 232). For this critical point which marks an *acceleration* instead of the *retardation* in the rate of

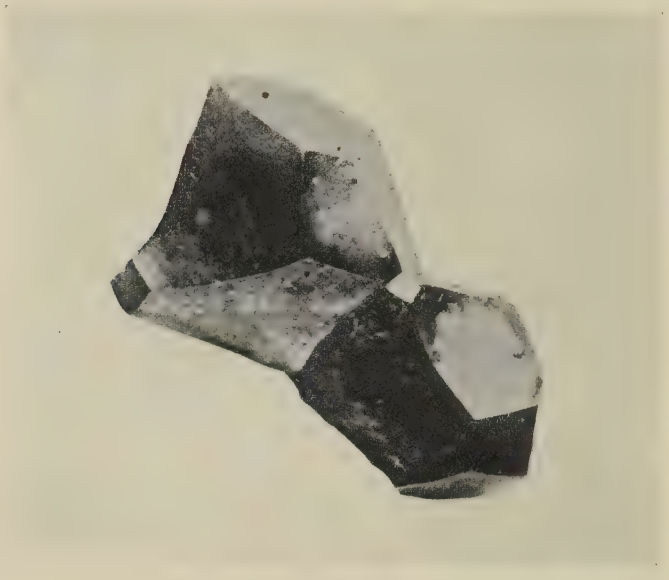


Fig. 238. — Single crystals. × 4.

heating generally occurring at the thermal critical point, Dr. Krivobok suggests, temporarily at least, the notation A_x. He finds that when the A_x transformation has once taken place, it cannot again occur on a second reheating (Fig. 233) and also, necessarily, that if the steel is annealed after cold working the A_x point is absent. It is logical to anticipate a relation between this point and the recrystallization of cold worked ferrite which is known to take place in that range of temperature. This relation clearly exists, as shown in Figures 234 and 235, illustrating the structure of a small ingot of a 0.50 per cent carbon steel (1) cast, cold worked, and reheated below the A_x point, and (2) cast, cold worked, and heated just above the A_x point.

The deformation resulting from cold working (Fig. 234) has caused an orientation of the ferrite particles parallel to the direction in which the casting was elongated, but it will be noticed that each ferrite area remains structureless, an indication that it has the same crystalline orientation throughout. On heating above the A_x point these ferrite masses break up into a number of grains (Fig. 235), as evidenced by the network which is now apparent.

The evolution of heat observed at the A_x temperature necessarily indicates a sudden change of internal energy which probably results from a relief of internal strains, this relief in turn causing recrystallization, hence the coincidence of the two

phenomena. Bearing in mind that the more severe the cold working the lower the temperature of recrystallization, it should be expected that after severe deformation, the A_x point will occur at a lower temperature.

Mechanism of Recrystallization after Cold Deformation. — Dr. Krivobok has very recently thrown a great deal of light on the mechanism of the grain growth of ferrite after deformation produced by hammering. ("A Photomicrographic Study of

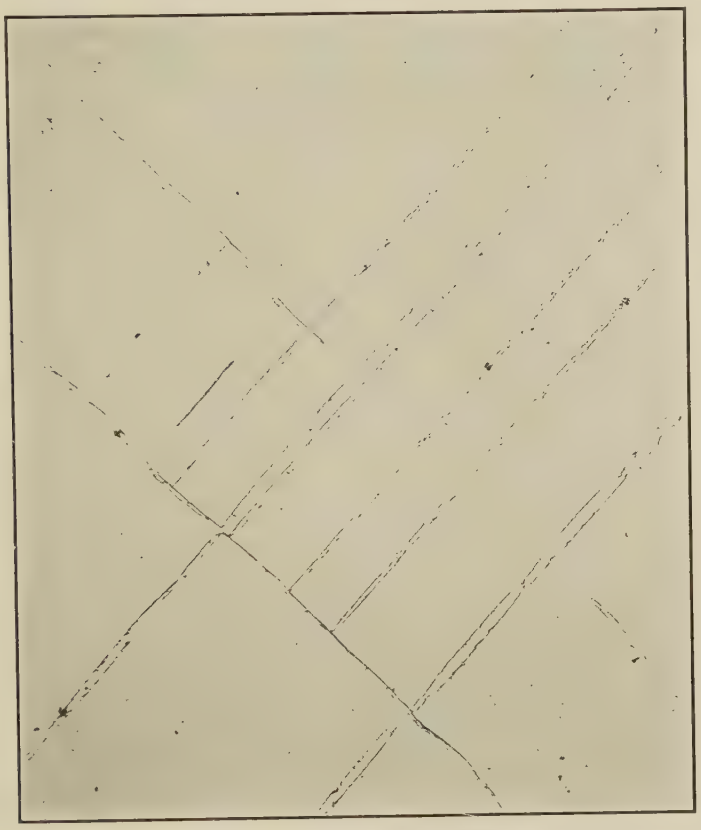


Fig. 239. — Single crystal, cold worked, unannealed. Etched HNO_3. × 200.

the Process of Recrystallization in Certain Cold Worked Metals," Am. Inst. Min. and Met. Engineers, February, 1926). Large single crystals of an iron-silicon alloy containing 1.76 per cent silicon (Fig. 238) were reduced by gentle and careful hammering at room temperature 25 per cent of their original thicknesses. The appearance of one such hammered crystal is shown in Figure 239. It will be seen to contain many parallel sets of double lines, and it was noted that frequently two series of such lines formed, crossing each other at right angles. As these lines reappear after polishing and etching, the author concluded that they could not be slip bands and rather than to describe them as mechanical twins or Neumann bands, he preferred to call them simply "markings." One set of these double lines is shown under a magnification of 3000 diameters in Figure 240 which reveals their "saw teeth" appearance. Upon reheating this hammered crystal to a suitable temperature the process of recrystallization could be followed as shown in Figures 241 to 246. It seems evident that the

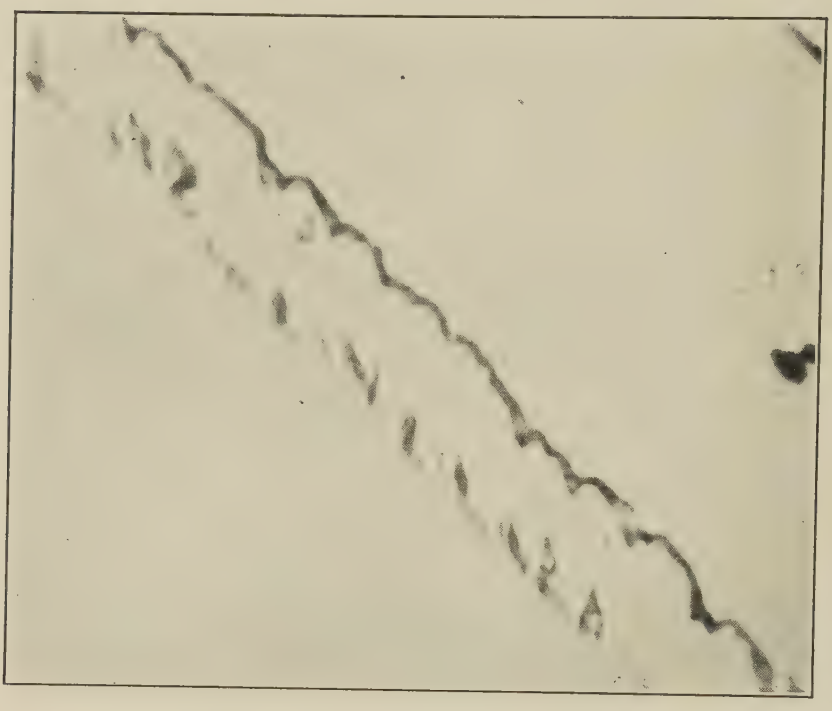


Fig. 240. — A part of a "marking." × 3000.

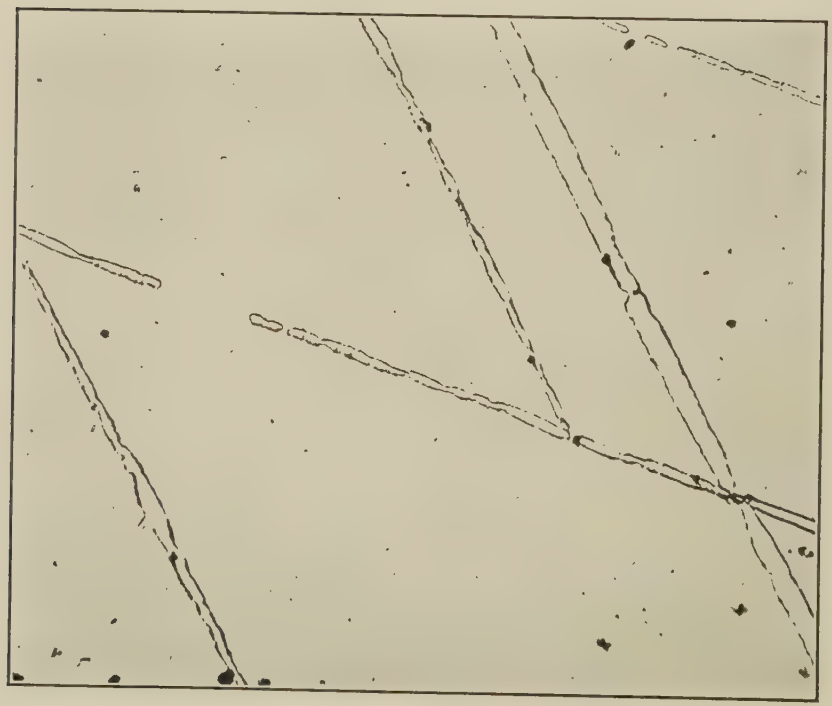


Fig. 241. — "Progressive" recrystallization in iron silicon alloy after cold working and heating. × 400.

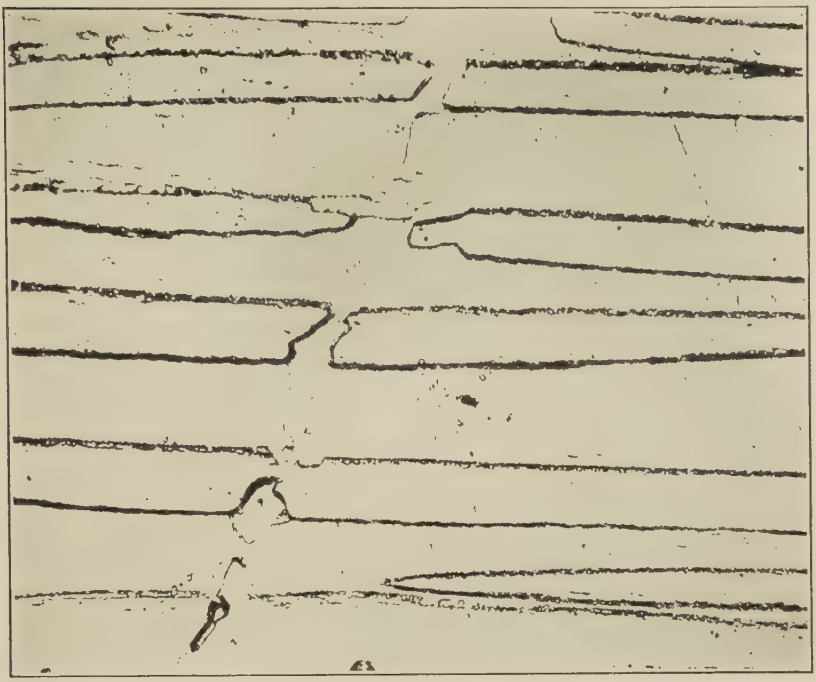


Fig. 242. — "Progressive" recrystallization in iron silicon alloy after cold working and heating. × 400.

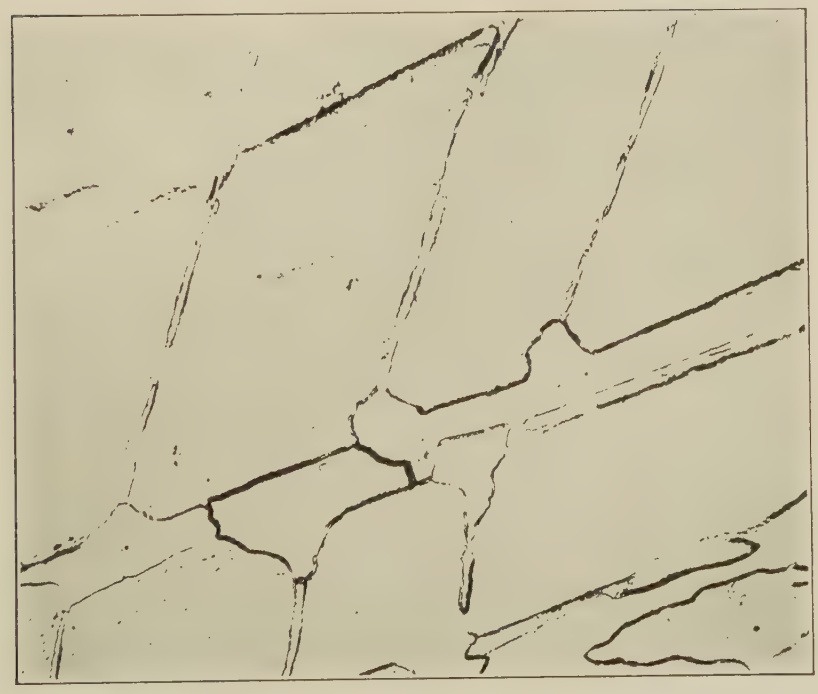


Fig. 243. — "Progressive" recrystallization in iron silicon alloy after cold working and heating. × 400.

Fig. 245. — "Progressive" recrystallization in iron silicon alloy after cold working and heating. × 400.

Fig. 246. — Totally recrystallized iron silicon alloy. × 400.

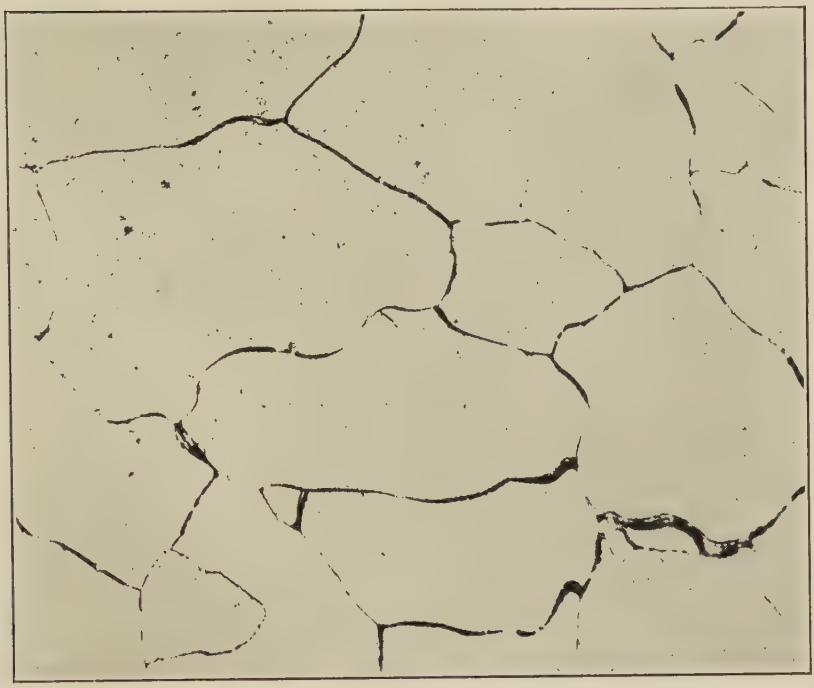


Fig. 247. — Structure of electrolytic iron after slight cold working followed by annealing. × 250.

Fig. 248. — Structure of same iron as in Fig. 247 after hammering. Etched HNO_3. × 450.

birth of new grains always starts at the markings, from which they gradually invade the surrounding (unstrained?) metal. The gradual widening and local bulging of the double lines, finally resulting in the production of equi-axed grains, should be noted.

Dr. Krivobok subjected to a similar treatment some electrolytic iron which had been annealed but not remelted. In order to increase the grain, it was slightly cold

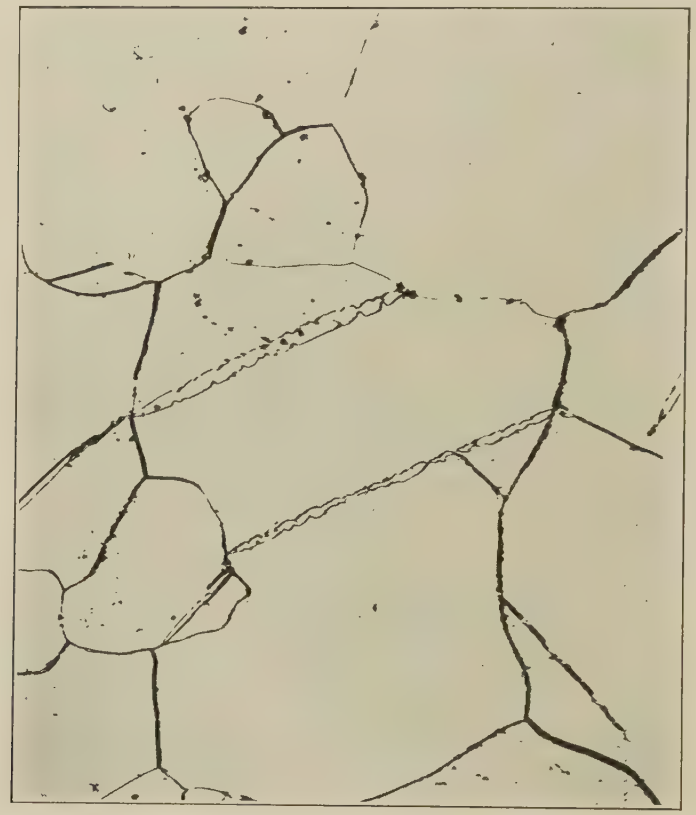


Fig. 249. — The structure of "markings." × 450.

worked and then annealed, its structure assuming the appearance shown in Figure 247. Its thickness was then reduced 25 per cent by gentle hammering at room temperature, when it was found that it contained many markings very suggestive of Neumann bands (Fig. 248). Heating this hammered electrolytic iron to 288 deg. C. for a half hour did not result in crystallization, but it was found that the markings now consisted of double parallel lines (Fig. 249) very similar to those observed in single crystals of iron-silicon alloys and that on heating to higher temperatures, recrystallization started and progressed also in the same manner (Figs. 250 to 252).

It seems probable that this disclosure of the mechanism of recrystallization will lead to further and fruitful investigation of this important field. It should be borne in mind that the effects of dynamic stresses only have been investigated by Krivobok, and it will be of great interest to ascertain whether recrystallization after deformation resulting from static stresses proceeds in a similar way.

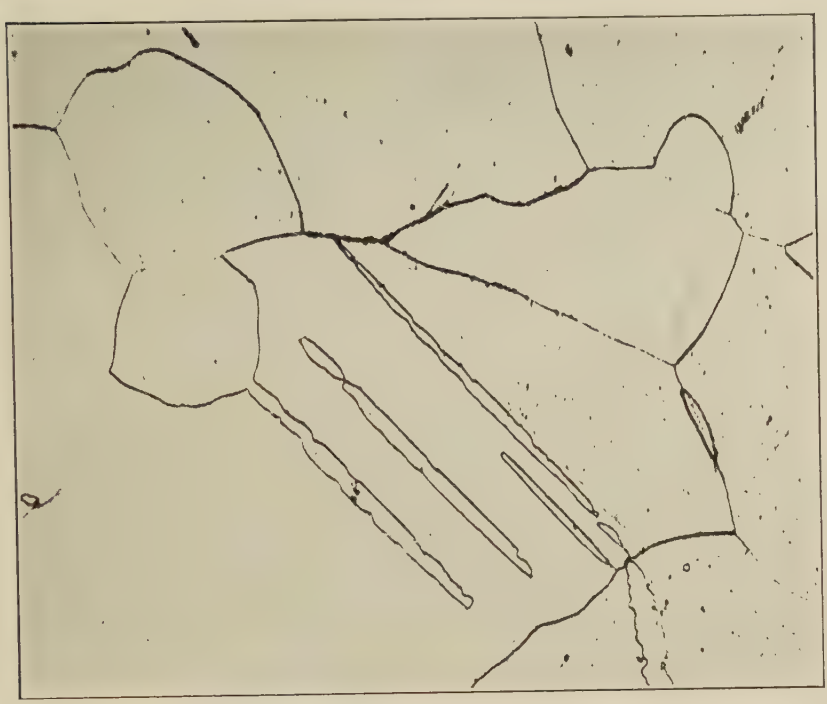


Fig. 250. — "Progressive" recrystallization in electrolytic iron after cold working followed by heating. Etched HNO_3. × 450.

Fig. 251. — "Progressive" recrystallization in electrolytic iron after cold working followed by heating. Etched HNO_3. × 450.

Brittleness of Low Carbon Steel. — The crystalline growths and other structural changes described in the foregoing pages lead naturally to the consideration of the brittleness occasionally exhibited by low carbon steel. Since steel containing very little carbon is essentially made up of ferrite, its occasional brittleness must be due to the occasional brittleness of ferrite, a constituent by nature soft and ductile. Stead

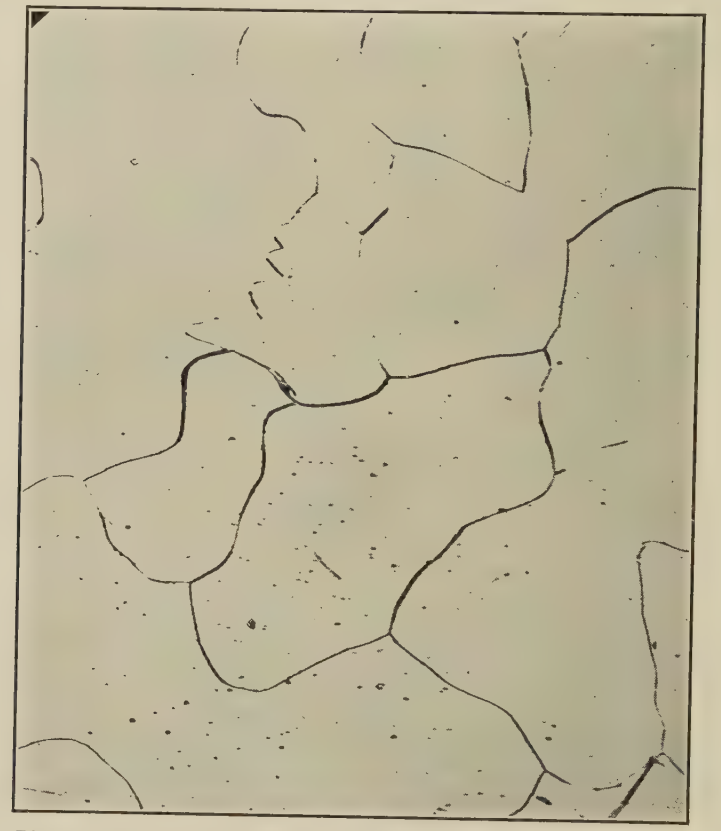


Fig. 252. — Complete recrystallization in electrolytic iron after cold working followed by heating. Etched HNO_3. × 450.

has indicated two kinds of brittleness from which ferrite may, and occasionally does, suffer, namely, (1) "inter-granular" brittleness and (2) "inter-crystalline" or "cleavage" brittleness.

By inter-granular brittleness is meant a lack of cohesion between the ferrite grains leading to ready fracture under shock, the line of fracture following the boundary lines of the grains. Such brittleness is usually due to the presence of impurities forming brittle and more or less continuous membranes surrounding the grains. The presence of much phosphorus, however, appears to produce inter-granular brittleness without producing surrounding membranes.

Inter-crystalline or cleavage brittleness is caused by the ferrite grains assuming *nearly* the same crystalline orientation so that the plane of fracture follows the cleavage planes and passes from grain to grain almost in a straight line. The diagram shown in Figure 253 will make this clear. The cross lines represent the cleavage planes in each grain. In *B* the metal is made up of large ferrite grains but the crys-

talline orientation of these grains is so heterogeneous that a line of fracture cannot readily be developed and pass from grain to grain, the abrupt change of crystalline orientation encountered at each boundary line acting as an effective obstruction to its advance. In *A*, on the contrary, while the grains are smaller they have nearly the same orientation, hence fracture may proceed from grain to grain with much greater ease and in a nearly straight line. Fortunately, so uniform a crystalline orientation is not often met with and cleavage brittleness is a rather rare occurrence. It can be cured by reheating the steel to 900 deg. or higher.

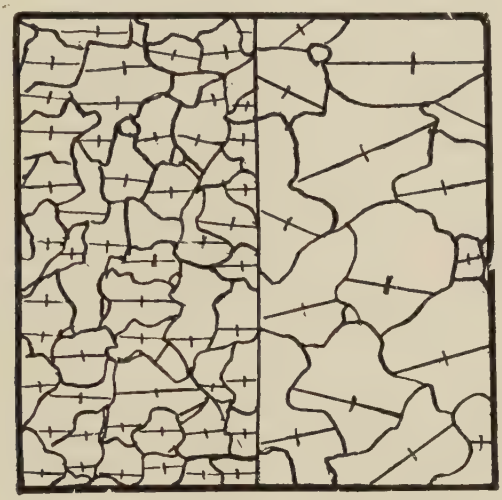


Fig. 253. — Crystalline orientation vs. Brittleness. (Stead.)

Stead also noticed that low carbon steel plates rolled below the critical range and, therefore, strained, and annealed likewise below the range, often exhibit a tendency to break in three directions, namely at 45 deg., to the direction of rolling, and at right angles with the surface of the plates, that is in the directions of the three cleavage planes of a cube having four faces at 45 deg. to the edges, and two faces parallel to the surface of the plates. This he calls "rectangular" brittleness. "We are led from this to conclude," Stead writes, "that, just as light impresses a latent image on a bromide photographic plate which cannot be seen but is developed and made manifest by the action of certain chemical agencies, so the rolling appears to impress a latent disposition in the steel to crystallize in certain fixed positions, and annealing develops it afterwards." The brittleness here referred to is undoubtedly caused by the crystalline growth of strained ferrite when annealed below its critical range, as fully explained in this chapter, the formation of large ferrite grains naturally causing brittleness. This kind of brittleness is sometimes called "Stead's brittleness." No very satisfactory explanation has so far been offered to account for this greater brittleness in certain directions. It may be that the large crystalline grains of ferrite produced have nearly the same orientation and that they are so oriented as to lead to easy inter-crystalline rupture in the directions indicated.

Spheroidizing of Cementite. — It is now well understood that on slow cooling through the critical range austenite of eutectoid composition is converted into well-

defined pearlite made up of distinct parallel plates or lamellæ alternately of ferrite and cementite, while in hyper-eutectoid steel the excess cementite tends to form at the boundaries of the pearlite grains and between the cleavage planes of the austenite. This condition of the cementite of pearlite as well as of the free cementite is not, however, final, not being structurally stable, for if the steel be kept for a sufficiently long time at a temperature but slightly below its critical range, preferably between 600 and 700 deg. C., the cementite shows a marked tendency to collect in the form of rounded particles embedded in a matrix of ferrite. The phenomenon has been called "spheroidizing" by Howe, or when restricted to the pearlite-cementite, "divorcing," on the ground that it constitutes a true divorce between the constituents of pearlite, namely ferrite and cementite. Pearlite that has undergone spheroidizing is sometimes called "granular" or "globular" pearlite.

Both hypo- and hyper-eutectoid steels are reported to spheroidize more readily than eutectoid steel, the free ferrite or cementite probably acting as nuclei. Even eutectoid steel, however, can be completely spheroidized if the heating be continued long enough. Howe states that the transformation is more rapid in a 0.21 per cent carbon than in a 0.59 per cent carbon steel. It seems probable that sorbite yields to the spheroidizing treatment more readily than true pearlite, from which it follows that for the purpose of spheroidizing the steel should first be made sorbitic. This can be done by relatively quick cooling through the critical range, or as already explained by very quick cooling through the range, thereby producing martensite or troostite, followed by reheating slightly below the critical range, which is also the temperature at which the spheroidizing operation should be conducted.

Howe and Levy state that both high heating and long heating above the range retard the divorcing of pearlite. Very slow cooling through the A_1 point sometimes suffices, while repeated cooling and heating through the A_1 point also promotes spheroidizing.

Babochine writes that in soft steel (0.20 per cent carbon) free cementite forms easily if the cooling through the Ar_1 point is 10 deg. per minute or slower. Ilyine advises heating 18 hours at 700 deg. C. for spheroidizing.

It is claimed by some that cold worked steel spheroidizes more quickly than unstrained metal. Whitely reports the complete spheroidizing of cold worked steel after two hours at 650 deg. C., a change which would require days in unstrained steel. The change according to this author begins at 500 deg. C., increasing with the temperature to some 680 deg. C. Stead also writes that hammering steel a little below the A_1 point by breaking up massive cementite helps spheroidizing in subsequent treatment. Quenched steels are also said to spheroidize more rapidly than unquenched metal, which amounts to saying that sorbite undergoes that change more readily than pearlite since, as already explained, the spheroidizing temperature is also the sorbitic range in reheated martensitic (hardened) steel. It has likewise been noted that finely lamellar pearlite granulates more readily than coarsely lamellar pearlite, which is consistent with the ease with which sorbite spheroidizes, it being permissible to consider sorbite as an extremely fine pearlite. The spheroidizing treatment greatly decreases the strength and elastic limit while increasing the ductility and softness, and also the resistance to wear (Abbott), these effects being more marked in high than in low carbon steels.

Hoyt assigns a tensile strength of 100,000 lbs. and an elongation of 11.8 per cent to lamellar pearlite against 76,500 lbs. and 19.75 per cent to granular pearlite.

Portevin indicates a Brinell hardness of 262 for lamellar pearlite and 137 for

spheroidized pearlite. The treatment therefore may be applied to soften steel, especially high carbon steel, in order to facilitate machining. The spheroidized structure after it has served its purpose may then be replaced by any other desired structure

Fig. 254. — Steel. Carbon 0.85 per cent. Magnified 1000 diameters. Spheroidized cementite. (E. H. Peirce.)

Fig. 255. — Steel. Carbon 1.10 per cent. Magnified 1000 diameters. Spheroidized cementite. (W. J. Burger, Correspondence student.)

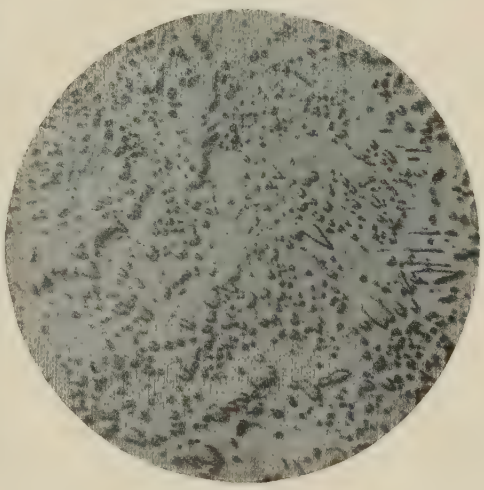


Fig. 256. — Steel. Carbon 1.24 per cent. Magnified 1000 diameters. Spheroidized cementite. (Osmond.)

through suitable heat treatment. According to Belaiew the patterns of Damascus steel and its remarkable physical properties are probably caused by a divorcing of ferrite and cementite in macroscopically visible masses produced by prolonged exposure to a temperature not exceeding redness.

Steel in the spheroidized condition is shown in Figures 254 to 256.

Graphitizing of Cementite. — It will be explained in another chapter that the carbide Fe_3C (cementite) is not the most stable form that can be assumed by carbon

when alloyed with iron. It will be shown that cementite tends to break up into iron and graphite according to the reaction

$$\underset{\text{cementite}}{Fe_3C} = \underset{\text{ferrite}}{3\,Fe} + \underset{\text{graphite}}{C}$$

and that the graphite form is the final stable condition of carbon. This graphitizing tendency of cementite remains latent unless the conditions be favorable to its activity. These conditions are: (1) long exposure to a temperature exceeding the critical range

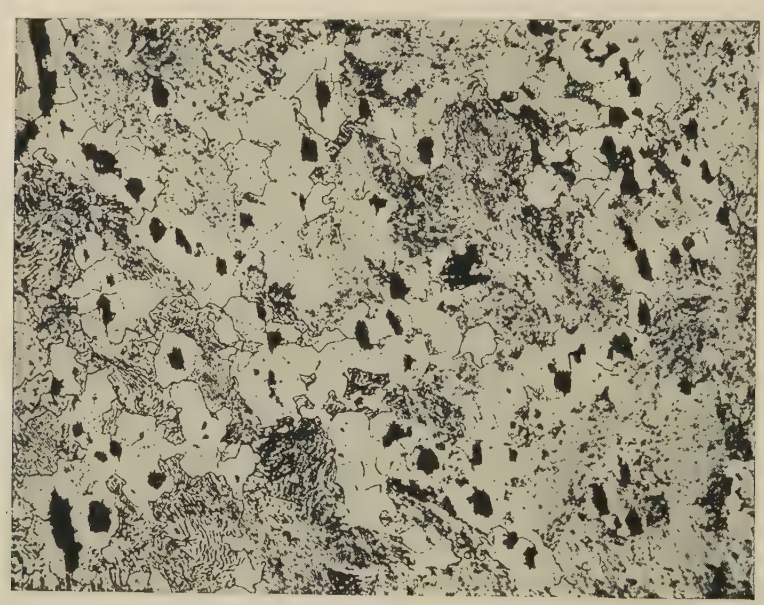


Fig. 257. — Steel. Carbon 1.25 per cent. Magnified 150 diameters. Annealed five hours at 830 deg. C. (C. C. Buck, Correspondence Course student.)

and slow cooling, (2) the presence of much carbon, and (3) the presence of silicon or of some other elements exerting a similar influence. It will be shown that this tendency of cementite to be converted into graphite and iron is responsible for the production of so-called malleable castings, and probably also for the production of gray cast iron. In the case of steel, because of the relatively small amount of carbon present (not exceeding 1.75 or at the most 2 per cent), the graphitizing tendency is slight. Long exposure of hyper-eutectoid steel, especially if it contains more than one per cent carbon, however, to a temperature exceeding its critical range, is always likely to produce a small amount at least of graphitic carbon, greatly impairing thereby, if not ruining, the metal. An instance of graphite formation in high carbon steel is shown in Figures 257 and 258. There is little doubt but the free cementite present in hyper-eutectoid steel, and formed as the steel cools from its Ar_{cm} to its $Ar_{3\text{-}2\text{-}1}$ point, is more readily converted into graphite than the cementite included in the pearlite. Once the graphitizing is started, however, it may be carried to completion and include the whole of the cementite present. This indeed is what happens in certain grades of malleable cast iron and of gray cast iron which contain practically

the totality of their carbon in the form of graphite. The presence of some free cementite appears to be necessary to start the graphitizing, which would explain why it

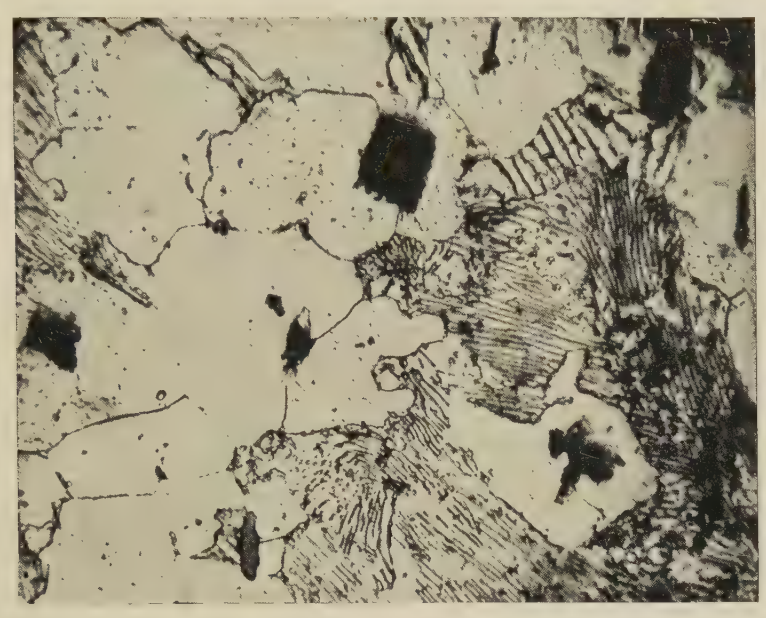


Fig. 258. — Steel. Carbon 1.25 per cent. Magnified 670 diameters. Annealed five hours at 830 deg. C. (C. C. Buck, Correspondence Course student.)

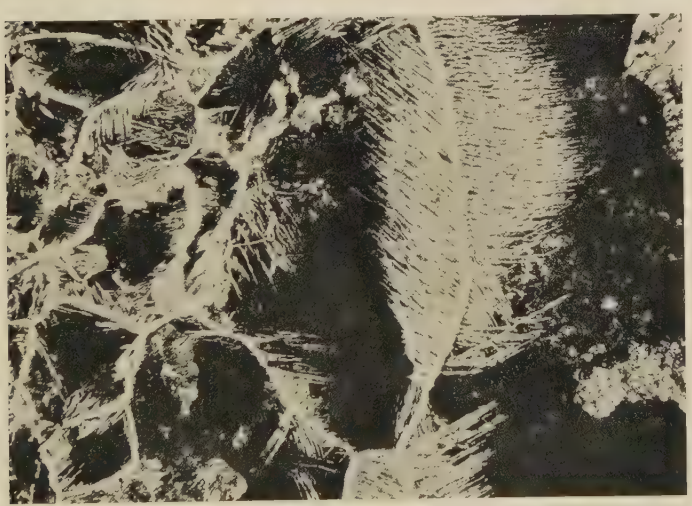


Fig. 259. — Steel. Carbon about 0.50 per cent. Heated to about 1100 deg. C. (P. J. Neely, Correspondence Course student.)

does not take place in hypo-eutectoid steel. The author at least never had a case of graphite formation in such steels brought to his attention nor was he ever able to produce graphite in hypo-eutectoid steel.

Overheating. — Long exposure of steel to a high temperature necessarily develops a very coarse structure and the metal is then said to have been overheated.

Stead describes the coarse crystalline structure of overheated steel containing from 0.20 to 0.50 per cent carbon as triangular arrangements of ferrite and pearlite, and that of steel containing from 0.50 to 0.70 per cent carbon as large ferrite cell walls and offshoots of ferrite penetrating the pearlite (Fig. 259). Overheating should not be confounded with burning: overheated steel can be readily restored to a normal condition by merely heating above the critical range, and is neither red-short nor cold-short, while burnt steel is extremely brittle.

Burnt Steel. — When high carbon steel is heated to a temperature approaching its melting point, it becomes extremely red-short as well as cold-short, while its frac-

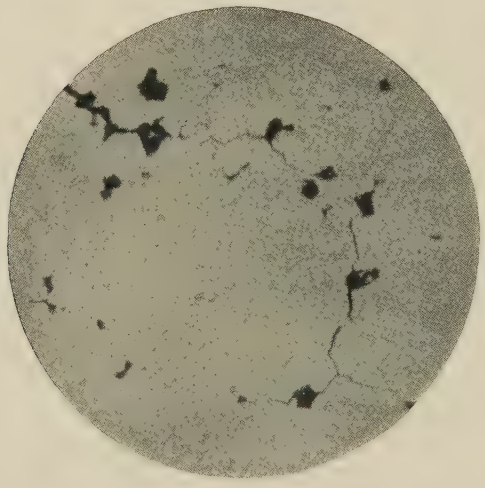


Fig. 260. — Burnt steel. Carbon 1.24 per cent. Magnified 20 diameters. Quenched at a white heat. Unetched. (Osmond.)

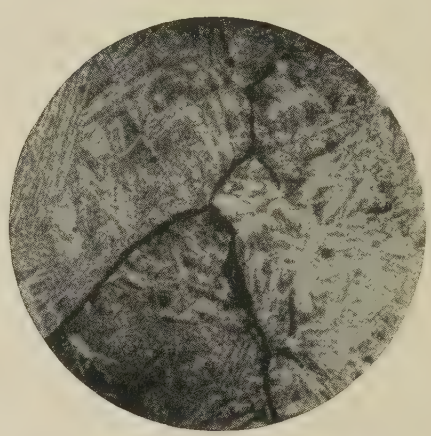


Fig. 261. — Burnt steel. Magnified 30 diameters. (Stead.)

ture becomes very coarse and shiny. The steel in such condition is said to be burnt. It was generally believed that the red-shortness of burnt steel could not be cured short of remelting, but Stead insists that if burnt steel be allowed to cool completely and is then reheated to a proper temperature it can be rolled and forged as well as if it had not been burnt. It is held by some that the burning of steel is due to the evolution of gases under the influence of a high temperature, chiefly carbon monoxide, resulting from atmospheric oxygen finding its way through the pores of the metal and combining with some of the carbon, although according to Howe other occluded gases, such as hydrogen and nitrogen, may also contribute. These gases force the crystalline grains apart, destroying their cohesion, hence the brittleness of the metal. Oxidized membranes are also frequently found surrounding some of the grains, their presence readily explaining the impossibility of restoring burnt steel by forging since they would prevent the welding of adjacent grains. Instances of the structure of burnt steel are shown in Figures 260 and 261. Howe defines burning as being "a mechanical separation of the grains on extreme overheating." Some writers have argued, apparently on good ground, that burning will not take place unless the steel has been heated to so high a temperature that it has actually begun to melt, the explanation being perfectly consistent with the well-known fact that high carbon steel burns much more readily than low carbon steel. To make the matter clear, let us con-

sider the diagram of Figure 262 in which the solidification period of steel is shown as influenced by its carbon content. This diagram will be discussed at greater length in another chapter. Let us for the present note (1) that as the carbon increases from 0 to 2.0 per cent the solidification of the steel is lowered from *A* to *B*, that is from 1500 deg. C. to 1325 deg., (2) that while carbonless iron solidifies at a constant temperature, namely 1530 deg., as the carbon increases the range of temperature covered by the solidification period increases likewise, extending from *B* to *C* with 2 per cent carbon, that is from 1325 to 1130 deg. C. *ABC* then represents the solidification zone of steels of increasing carbon content, and the heating of the metal to any point

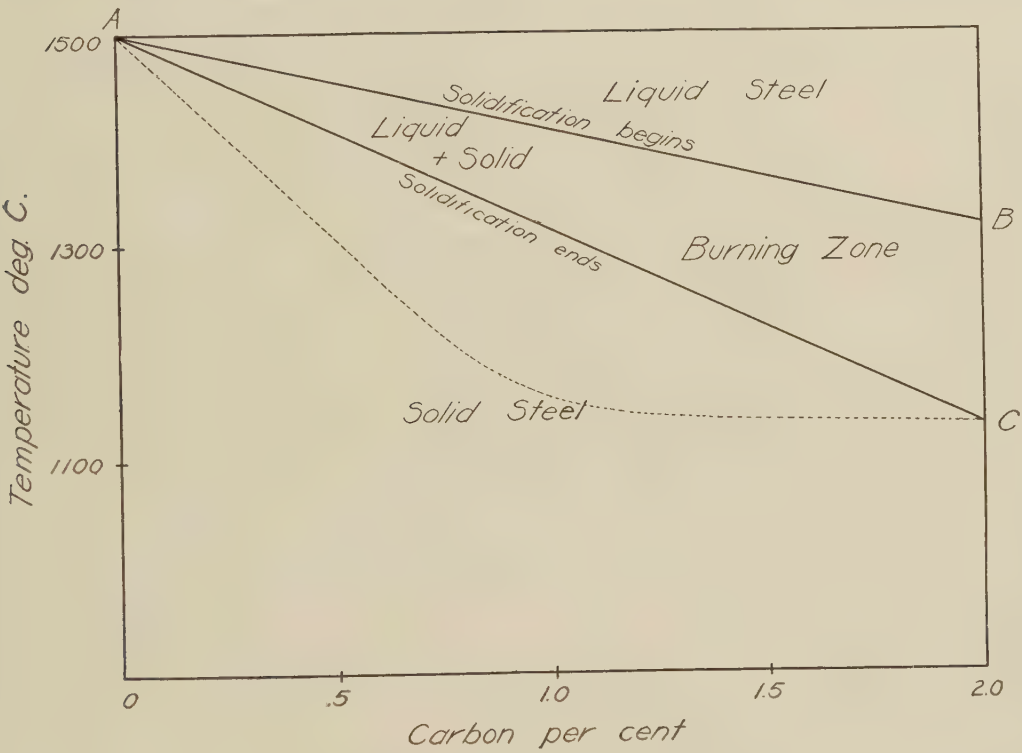


Fig. 262. — Diagram depicting the burning temperature range.

within this zone, when it is partly melted, will cause it to burn. It follows from this that carbonless iron and very low carbon steel can be heated to a very high temperature without burning, while the danger of burning increases with the carbon. With 0.50 per cent carbon, for instance, the burning zone extends from 1400 to 1450 deg., with 1.0 per cent it extends from 1310 to 1400 deg., with 1.50 per cent carbon from 1210 to 1360 deg. In short, as the carbon increases the steel burns more readily (1) because its melting point is lowered and (2) because its solidification zone, which is also its burning zone, is widened. According to the theory it should not be possible to burn carbonless iron, and indeed the author does not know that the claim has ever been made that carbonless iron could be burnt.

If *ABC* represents a burning zone into which steel cannot be brought without having its useful qualities destroyed, we naturally ask why all steels are not so injured, seeing that they must pass at least once through this zone in cooling from the

molten condition. The reason why steel does not burn on solidifying and further cooling is explained by Howe on the ground that while steel ingots or other castings solidify, much hydrogen is given out which may mechanically restrain the oxygen from entering and also counteract it, preventing thereby the evolution of CO from within and the formation of oxidized films, the chief causes of burning. It is also possible, Howe says, that the greater kneading which an ingot undergoes cures burning, while the slight kneading possible in reworking a steel bar does not. This, however, would not explain why steel castings, which undergo no work at all, are not

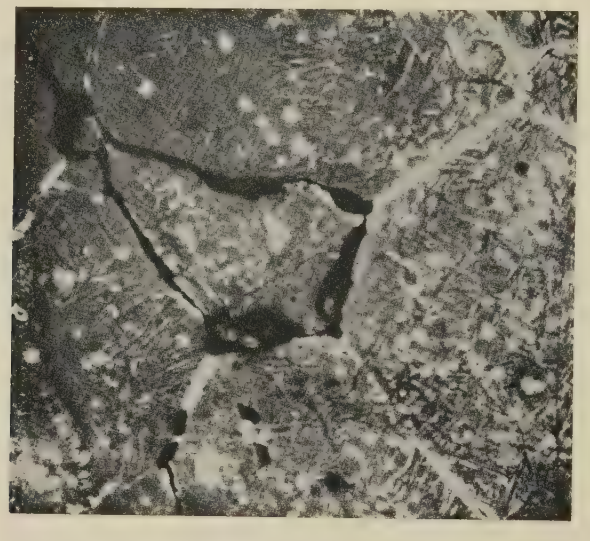


Fig. 263. — Burnt steel etched with Stead's cupric reagent showing globules and envelopes rich in phosphorus. Magnified 50 diameters. (Stead.)

burnt, unless it is because they are generally protected from atmospheric oxidation by their molds.

Overheating results from heating close to but below AC (Fig. 262), generally for a considerable length of time, while, as explained, the temperature in burning is carried above AC.

Important results obtained by Gutowsky would place the end of the solidification of various carbon steels as indicated by the dotted line in Figure 262. If these are the correct temperatures at which solidification is complete, it follows that the burning zone is wider than was generally believed before the publication of these results.

Stead, rejecting the oxidizing gases theory, believes that the burning of steel resulting from heating the metal to incipient fusion, causes the formation of globules or envelopes rich in phosphorus (hence fusible) round the crystals and that their presence or absence is a proof of the steel having been burnt or not. When they occur they are readily detected by etching the metal with his cupric reagent.

The burnt steel in Figure 263 has been etched with this reagent. The white network and white particles show the segregation of portions rich in phosphorus. Stead writes:

"The question is often asked of the expert, when steel samples have broken up at the rolls, whether the material is naturally red-short or has been burnt. The sides of cracks found in the steel, whether simply red-short or burnt, are always lined with oxide; and the expert, in conducting his examination, must be careful to select portions free from cracks and to polish and etch them. If they be free from globular specks rich in phosphorus, it may be concluded that the material has not been burnt and is naturally red-short, but if such specks be present the reverse conclusion will be justified."

CHAPTER XVIII

THE CEMENTATION AND CASE HARDENING OF STEEL

The affinity of iron for carbon is so great that when heated to a sufficiently high temperature in contact with some suitable carbonaceous matter it readily absorbs some of that element. If the heating be protracted (several days) and the amount of carbon absorbed considerable, the operation is known as "cementation" and the resulting metal as "cemented," "converted," or "blister" steel, or in Sheffield, England, as "blister bar," while if the treatment be of relatively short duration (a few hours) and the absorption of carbon in consequence superficial, it is called "case hardening."

Cementation is generally applied to wrought-iron bars which are afterwards melted (crucible process) and shaped into finished articles by casting or forging, while case hardening is applied directly to finished objects generally of low carbon steel. The purpose of cementation is to introduce carbon into wrought iron, thereby converting it into steel, the subsequent treatments (melting, forging) producing a uniform distribution of the carbon, whereas the purpose of case hardening is to manufacture steel objects with hard skins or cases while retaining their soft and tough centers or cores.

The quantity of carbon thus absorbed by iron at a high temperature but below its melting point depends chiefly upon (1) the composition of the iron or steel subjected to carburizing, (2) the carburizing temperature, (3) the length of time at that temperature, and (4) the nature of the carburizing material.

Composition of the Iron or Steel Subjected to Carburizing. — It is probably true that the smaller the proportion of carbon in the iron the more eagerly will it take up carbon, from which it follows that as the carburizing proceeds, that is as the metal becomes more highly carburized, additional introduction of carbon requires progressively longer time, the metal acting in this way not unlike a solution approaching its saturation point.

In the cementation process bars of very pure wrought iron and in "case hardening" steel objects containing at the most 0.20 per cent carbon are subjected to the carburizing treatment. The steel should not generally contain over 0.40 per cent of manganese lest the case be too brittle. Certain elements appear to hinder the carburizing operation while others facilitate it.

According to Guillet the absorption of carbon is favored by those special elements which exist as double carbides, such as manganese, tungsten, chromium, molybdenum, and opposed by those which form solid solutions with iron, such as nickel, silicon, and aluminum.

Carburizing Temperature. — Cementation and case hardening require (1) the formation of Fe_3C and (2) its solution in iron. While the first requirement may be

met, although very slowly, below the critical range, for the second the iron must be heated above the range, because alpha iron has little if any dissolving power for carbon. In order to produce quick and intense carburization the iron should be in its gamma condition, and steel, therefore, in the condition of a solid solution. Cementing and case-hardening operations must consequently be conducted above the critical range of the iron or low carbon steel treated, that is at a temperature exceeding 825 deg. C. It is also certain that the higher the temperature the quicker will carbon be absorbed and the deeper will it penetrate into the steel, that is the deeper the "case." At Sheffield, England, where the cementation process is used more extensively than anywhere else, the carburizing temperature is in the vicinity of 950 to 1000 deg. Most case-hardening treatments are probably conducted in the vicinity of 900 to 950 deg. C.

Time at Carburizing Temperature. — The amount of carbon absorbed, and therefore the thickness of the case as well, increases, of course, with the length of the operation, but as already mentioned, carburization takes place more and more slowly as the carbon content increases. The maximum amount of carbon which iron can take up and dissolve while in the solid state is probably not far from 2.50 per cent, this, however, requiring a protracted treatment at a very high temperature. While in the manufacture of blister steel considerably more than 1 per cent of carbon is frequently introduced into the wrought-iron bars, in carburizing finished steel articles it is seldom desired to produce a case containing more than 1 per cent of carbon near the outside, a superficial, carburized layer of eutectoid composition (0.85 per cent C.) being generally considered to yield the best results. The length of time needed to produce the desired degree of carburization and desired depth of case must necessarily depend upon the nature of the metal, the kind of carburizing material used, and the temperature.

Distribution of the Carbon. — It will be apparent from the nature of the operation that in this carburizing of solid iron carbon travels slowly from the outside towards the center and that, therefore, the proportion of carbon absorbed must decrease from outside to center, unless indeed the objects treated are very thin or the treatment so long and conducted at so high a temperature as to cause even the center to absorb the maximum amount of carbon. The decrease of carbon as one approaches the core of the object is well illustrated in Figures 264 and 265. A band of hyper-eutectoid steel characterized by the presence of free cementite is frequently noted (Fig. 264), followed by a band of eutectoid composition characterized by the absence of both free cementite and free ferrite, and this in turn is followed by a band showing abrupt and rapid decrease of carbon characterized by an increasing amount of free ferrite.

In case-hardening operations the penetration of the carbon may be very slight indeed, not exceeding 0.5 mm., while it may measure as much as 5 mm. In the majority of instances the penetration does not exceed 2 mm. This depth of penetration or thickness of case must be regulated according to requirements. It will depend upon temperature, time, composition of steel, and kind of carburizing material. Lake mentions 0.87 mm. per hour as an average speed of penetration.

The production of a deep case, while at the same time keeping the carbon content of the outside of the case below 1 per cent, may be brought about by a rather long treatment at a relatively low temperature, namely, some 850 deg. C. Some results obtained by Guillet in regard to the influence of temperature and of time on the

depth of penetration are shown graphically in Figure 266 as plotted by Bauer. The carburizing material used was not stated. The full line represents relative penetra-

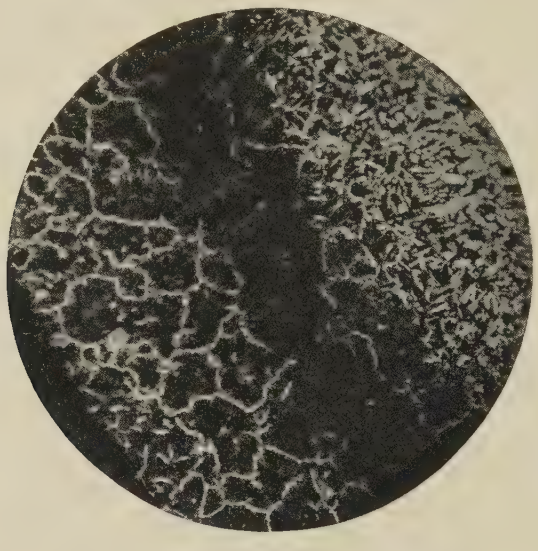


Fig. 264. — Steel, case hardened. Magnified 20 diameters.

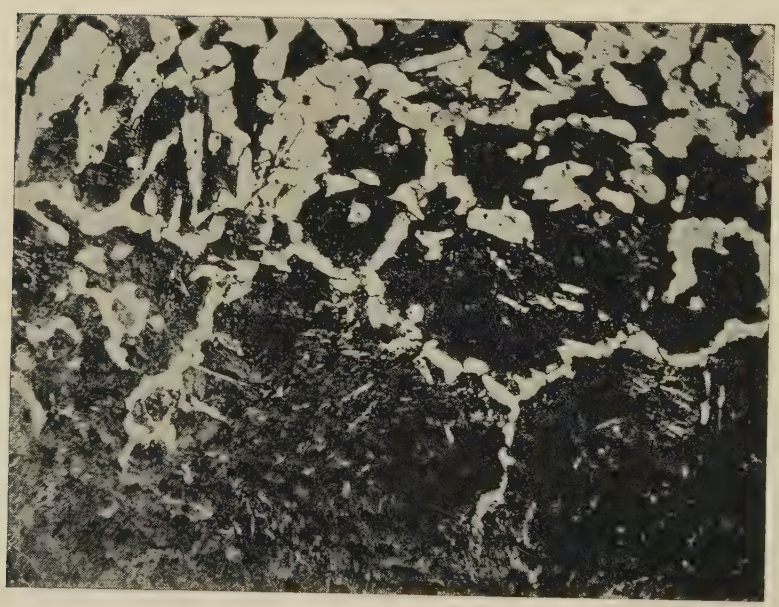


Fig. 265. — Steel, case hardened. Magnified 100 diameters. (G. A. Reinhardt, in the author's laboratory.)

tions at 1000 deg. after different lengths of time, namely, one, two, four, and six hours, while the broken line represents the depths of penetration resulting from heating for eight hours at different temperatures.

As already stated, it is not generally advisable to produce cases containing over

0.90 per cent carbon unless the excess cementite be prevented from separating through suitable heat treatment, that is by quenching from above the Ar_{cm} point. If free cementite be allowed to form, it generally assumes the form of a network (Fig. 264), which in turn causes chipping and flaking. The high quenching temperature necessary to remove the undesirable cementite network implies coarser grains, more severe strains, and greater danger of cracking. It is better, therefore, if possible, to prevent the absorption by the iron of more than some 0.90 per cent carbon. For successful and sufficiently rapid commercial case hardening, the temperature cannot be materially inferior to 900 deg. C. At that temperature, however, iron

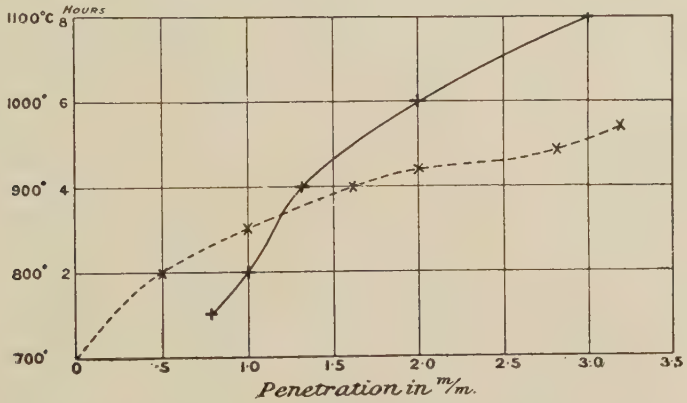


Fig. 266. — Temperature and time-penetration curve. (From Brearley's "The Heat Treatment of Tool Steel.")

may absorb considerably more than 1 per cent carbon. This might be prevented by heating to 900 deg. C. so that the iron may be in its gamma condition, when it absorbs carbon readily, followed by a gradual lowering of the temperature to some 800 deg C. or even lower. This is now permissible because as the iron dissolves carbon its upper critical point is lowered and it remains in the gamma condition at considerably lower temperatures. The formation of a hyper-eutectoid case should be hindered by this method, and a finer structure obtained because of the lower carburizing temperature.

It will be obvious that the process of case hardening can be controlled by the microscopical examination of test pieces much more readily and accurately than by chemical analysis.

Carburizing Materials. — A great variety of carbonaceous materials is used for introducing carbon in iron and steel in the solid state. These substances may be solid, liquid, or gaseous. Solid materials are used more extensively than liquid or gaseous ones, the most important being charcoal (both wood and bone), charred hoofs and leather, crushed bone, horn, beet-sugar pulp, mixtures of barium carbonate (40 per cent) and charcoal (60 per cent) or of salt (10 per cent) and charcoal (90 per cent), both recommended by Guillet, and for quick but very superficial hardening, powdered potassium cyanide and potassium ferro-cyanide or mixtures of potassium ferro-cyanide and potassium bichromate. A molten bath of potassium cyanide heated to 850 deg. and in which the steel articles are immersed quickly, produces superficial but hard and even cases. The poisonous character of the escaping gases,

however, is a serious objection to the use of this method. The carburizing of iron may also be performed at the proper temperature by means of gases such as illuminating or other coal or oil gases rich in carbon monoxide and in hydrocarbons. At the Krupp works in Germany gases are used for carburizing the faces of armor plates. Abbott states that out of 100,000 tons of carburizing material used in the United States in 1911, 85 per cent was granulated bone.

The relative merits of wood charcoal, charred leather, and a mixture of barium carbonate and of wood charcoal for carburizing are shown graphically in Figure 267, in which are plotted some results obtained by Shaw-Scott. While wood charcoal causes a slow carburization it is the best material and the one invariably employed for the production of very deep cases, as, for instance, in making blister steel.

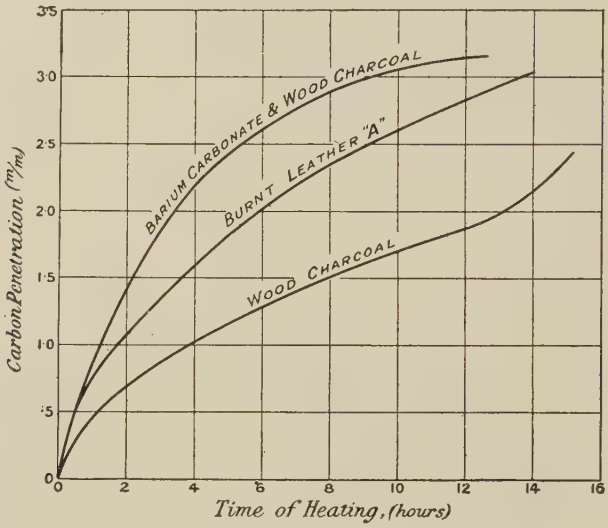


Fig. 267. — Time-penetration curve. (From Brearley's "The Heat Treatment of Tool Steel.")

Giolitti surrounds the pieces to be case hardened with charcoal and then passes through the annealing box carbon monoxide or carbon dioxide gas, the latter upon coming in contact with red-hot charcoal being converted into carbon monoxide ($CO_2 + C = 2\,CO$), which gas as later explained is the most active agent in carburizing. In Giolitti's opinion, however, CO when used alone generally fails to introduce enough carbon, but becomes much more effective when mixed with hydrocarbons, or better still with finely divided solid carbon. Under these conditions the maximum concentration does not exceed 0.90 per cent carbon even after eight hours at a *constant* temperature between 900 and 1100 deg C. If the temperature be permitted to fluctuate, however, between 1000 and 1100 deg., the outer layers take up as much as 1.10 per cent carbon after an annealing of 3 hours' duration.

Many so-called secret mixtures are offered for sale as case-hardening substances for which extraordinary virtues are claimed, the usual statement being that by their use steel of ordinary or inferior quality may be converted into high-grade metal comparable to the best crucible tool steel. On investigation they are generally found to be chiefly mixtures of carbonaceous and cyanogen compounds possessing the well-known carburizing properties of those substances.

Case Hardening by Gas under Pressure. — Dr. F. C. Langenberg has conducted in the author's laboratory an extensive series of experiments dealing with the case hardening of American ingot iron with various gases under varying conditions of temperature, time, flow of gas, and pressure. Some of the most conclusive results obtained will be recorded.

Illuminating gas of the following composition:

Hydrogen	40.10 per cent	Oxygen	0.58 per cent
Methane	26.10 " "	Carbon monoxide	11.38 " "
Nitrogen	14.04 " "	Heavy hydrocarbons	4.95 " "
Carbon dioxide	1.64 " "		

was passed through a tube furnace electrically heated and containing near the inlet end a plug of finely divided charcoal and, immediately following, small cylinders

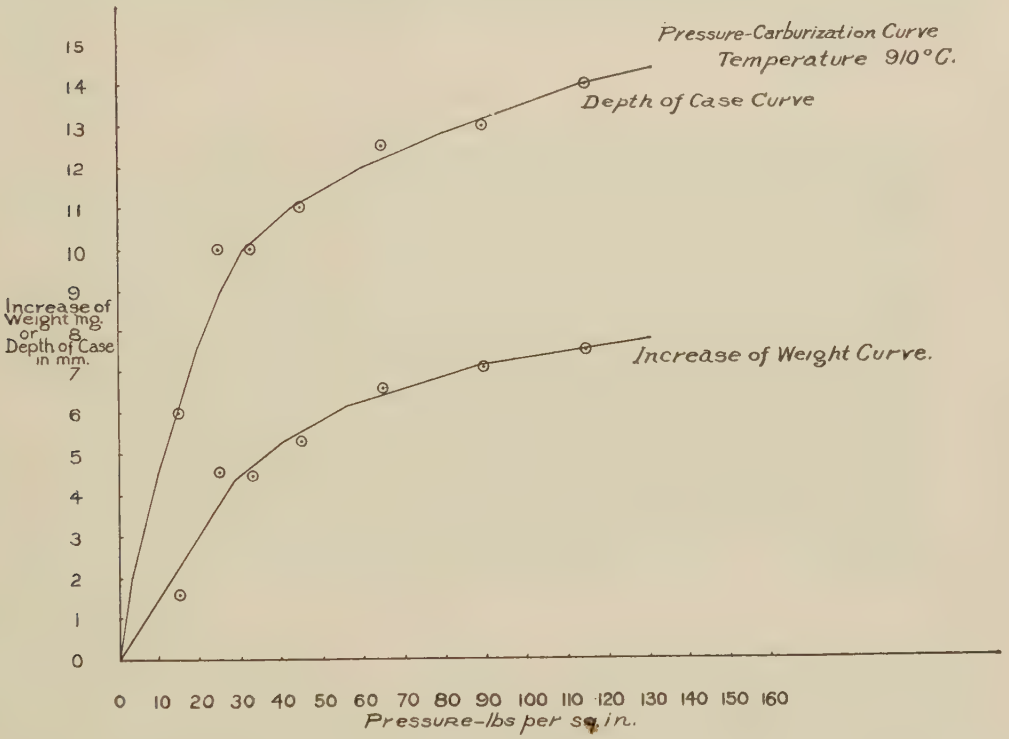

Pressure-Carburization Curve
Temperature 910°C.
Depth of Case Curve
Increase of Weight Curve.
Increase of Weight mg. or Depth of Case in mm.
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
Pressure-lbs per sq. in.

Fig. 268. — Case hardening by gas. Pressure-penetration curve. (F. C. Langenberg, in the author's laboratory.)

of American ingot iron to be case hardened. The passing of the illuminating gas through the highly heated charcoal converted the CO_2 originally present into CO ($CO_2 + C = 2\,CO$) and may also have produced some changes in the hydrocarbons present. It is not probable that the hydrogen content was greatly, if at all, affected. Maintaining the flow of gas constant at 5 liters per hour, the temperature likewise constant at 990 deg. C. for 3 hours, but varying the pressure from 0 to 115 lbs. per sq. in., a gradual increase in the carbon absorbed was observed, as indicated both by increase of weight and depth of case. This is clearly shown by the curves of Figure 268. It will be noted that the increase is greatest as the pressure rises from 0 to some

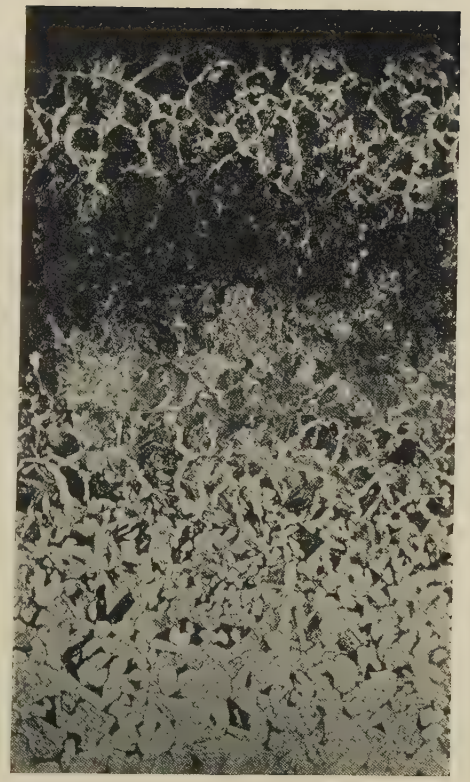


Fig. 269. — Pressure 26 lbs. per sq. in.

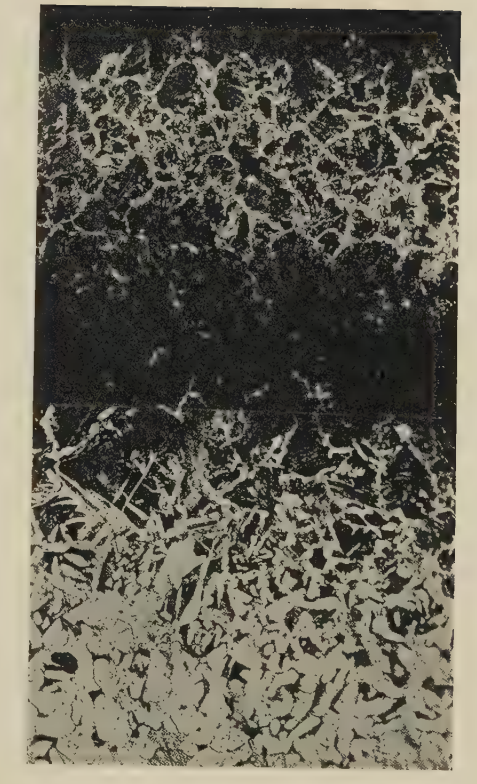


Fig. 270. — Pressure 45 lbs. per sq. in.

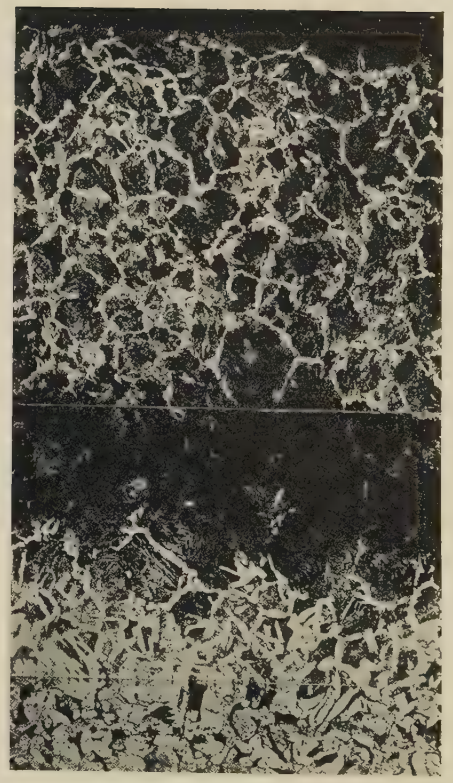


Fig. 271. — Pressure 75 lbs. per sq. in.

Case hardening by gas under increasing pressure. Temperature 990 deg. C. Time 3 hours. Flow of gas, 5 liters per hour. All photomicrographs are magnified 100 diameters. (F. C. Langenberg, in the author's laboratory.)

40 lbs. per sq. in., both curves for higher pressure showing a tendency towards a horizontal deflection. This occurrence was found to be still more marked when the case-hardening operation was conducted at lower temperatures. In every instance, however, the bend in the curves occurred in the vicinity of 40 lbs. pressure. The photomicrographs (Figs. 269 to 271) clearly reveal the increasing depth of case resulting from increasing gas pressure, other conditions remaining unchanged. It should be observed that it is the hyper-eutectoid portion of the case which is chiefly

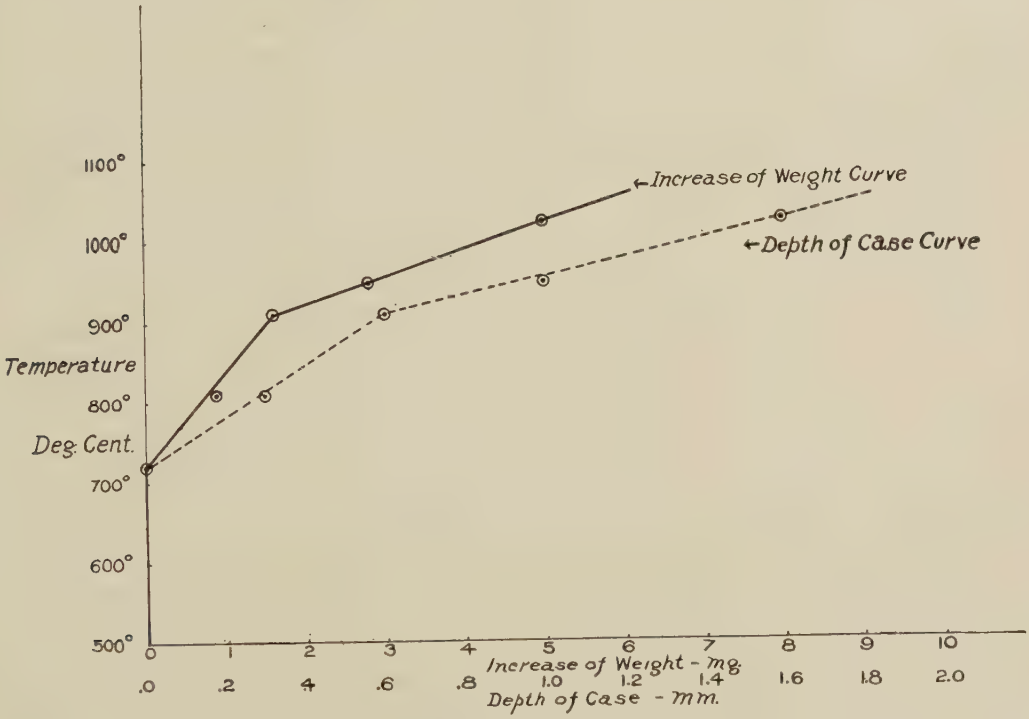


Fig. 272. — Case hardening by gas. Temperature-penetration curves. (F. C. Langenberg, in the author's laboratory.)

affected, increasing in thickness with the pressure, while the width of the eutectoid band remains practically the same.

Maintaining a constant atmospheric pressure, constant flow of gas (5 liters per hour), constant time (3 hours), but varying the temperature from 600 to 1000 deg. C., the curves of Figure 272 were obtained. They indicate the increasing amount of carbon taken up as estimated both by increasing weight and increasing depth of case. The following inferences appear justified: (1) at 700 deg. C. or at any lower temperature there was no absorption of carbon whatever, from which it may be concluded that α iron, under the prevailing experimental conditions, cannot dissolve carbon; (2) at 800 deg. C. there was a noticeable carbon absorption, hence the power to dissolve carbon is acquired between 700 and 800 deg. C., that is during the range of temperature where β iron also is formed, and it may be reasonably believed that the two occurrences are closely linked; (3) at 900 deg. there is a break in both curves indicative of a slower rate of increase, and this appears to be closely related to the formation of γ iron.

Figure 273 shows the structure of American ingot iron after the case-hardening operation just outlined conducted at 720 deg. C., while when performed at 810 deg. C.

Fig. 273. — American ingot iron case hardened by gas for 3 hours at 720 deg. C. Magnified 100 diameters. (F. C. Langenberg, in the author's laboratory.)

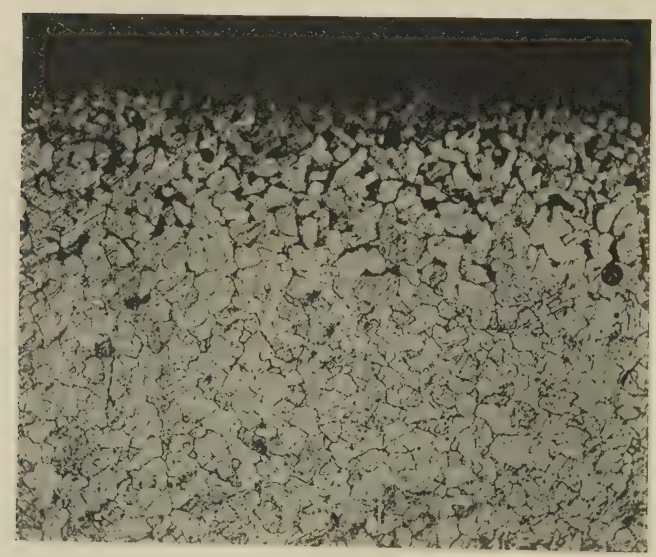


Fig. 274. — American ingot iron case hardened by gas for 3 hours at 810 deg. C. Magnified 100 diameters. (F. C. Langenberg, in the author's laboratory.)

the structure of the same metal was as represented in Figure 274. There is no indication of the former having absorbed any carbon while the carburizing of the latter is very appreciable.

Mechanism of Cementation. — It was held for many years that in the cementation of iron solid carbon passed bodily from the packing material into the metal, followed by a slow migration towards the center. Recent investigations, however, have made it evident that the transfer of the carbon from the packing material to the metal is accomplished chiefly, if not altogether, by means of some gases liberated or formed during the annealing treatment. It has been shown quite conclusively, for instance, that if a piece of steel surrounded by pure carbon be heated in vacuum, thus precluding the formation of gases, it will not take up carbon, although one observer has noted that if decided pressure be applied some carbon will pass into the iron even in the absence of gases. Whether this be so or not it is apparently certain that the carbon must first be volatilized before becoming very active as a carburizing agent in the cementation and case-hardening treatments.

Carbon monoxide (CO) and volatilized cyanogen (CN) compounds are the gases which seem most effective. The carbon monoxide is derived from a partial combustion of the carbon of the cementing material by atmospheric oxygen while the cyanogen results from a combination of that carbon with atmospheric nitrogen or from the decomposition of cyanide compounds such, for instance, as potassium cyanide and ferro-cyanide. It may be assumed that the carbon monoxide once formed gives up its carbon to the iron according to the reaction,

$$2\,CO + 3\,Fe = Fe_3C + CO_2,$$

the resulting Fe_3C or cementite being dissolved by the austenite very much as salt is dissolved in water and the CO_2 being again reduced to CO on coming in contact with fresh carbon ($CO_2 + C = 2\,CO$). The air necessarily present in the carburizing gases suffices, therefore, to supply the oxygen needed for the formation of some carbon monoxide. The marked activity of cyanogen compounds compared to the slower action of charcoal have led some to believe that cyanogen gases are especially effective in carburizing iron. It should be noted, however, that while cyanide compounds produce a much quicker carburization they soon lose their carburizing power so that when deep cases are needed, as in the manufacture of blister bars, charcoal, acting chiefly through the production of carbon monoxide, is preferable.

Cooling from Carburizing Temperature. — It is generally desired that articles subjected to the case-hardening treatment should have a very hard surface. To produce this hardness the case-hardened articles should be quenched from above their critical range. The prolonged heating at a very high temperature to which these articles have been exposed, however, has developed a coarseness of structure both in the core and in the case which would be retained if they were, as they sometimes are, quenched from the carburizing temperature or after cooling to a somewhat lower temperature. It is obvious that in order to impart a fine structure both to the core and to the case the articles should be cooled and then subjected to suitable heat treatments.

Heat Treatment of Case-Hardened Articles. — In order to refine the structure of the core which has been coarsened by a long exposure to a high temperature the metal should be reheated slightly above the critical range of that core, and since its carbon content seldom exceeds 0.15 per cent carbon a temperature of at least 900 deg. C. should be used. Guillet recommends 1000 to 1025 deg. The finer structure thus imparted to the core will then be retained most effectively by quenching the metal in water or oil. By such treatment, however, the case, although hardened, is

still relatively coarse since its quenching was effected at a temperature considerably exceeding its critical range. In order to refine it while leaving the structure of the core undisturbed the article should now be reheated slightly above the critical range of the case, that is to some 775 or 825 deg. C., and then quenched in oil or water. By this double treatment we have hardened the case while conferring to it as well as to the core a fine structure.

It has been observed that the low carbon steel cores of case-hardened articles are frequently coarser than the same steel after like heat treatment conducted in the absence of carburizing material. This is generally ascribed to the action of hydrogen, most carburizing agents evolving some of that gas at the annealing temperature. This increased coarseness of the cores of case-hardened implements is an additional reason why their structure should be refined by suitable heat treatments.

Tempering Case-Hardened Steel. — The properties of quenched case-hardened steel may often be further improved by tempering, i.e. by reheating to some 150 to 300 deg. C., in order to toughen the case and remove strains while losing but little hardness.

Carburization of Iron Below its Critical Range. — It has been shown by several investigators that pieces of iron or of low carbon steel exposed for long periods of time to the action of blast-furnace gases have become intensely carburized, from which it must be concluded, since the temperature of those gases remains substantially below the A_1 point, that carbon can combine with alpha iron to form the carbide Fe_3C at temperatures lower than A_1. It is not to be assumed, however, that much, if any, of this carbide will dissolve in the iron, since the latter is now in the alpha form, when its solvent power for carbon is practically nil. T. H. Byrom mentions a soft steel sheet exposed to blast-furnace gases for several years at a temperature of 500 deg. C. which was entirely converted into the carbide Fe_3C. This was probably due to the action of CO in the gases, assisted by the presence of catalyzers, as shown in a two steps reaction in the following equation:

$$\begin{aligned} 2\,CO + 3\,Fe + \text{catalyzer} &= CO_2 + C + 3\,Fe + \text{catalyzer} \\ &= CO_2 + Fe_3C + \text{catalyzer} \end{aligned}$$

This author further reports that at 400 deg. C. he obtained no carburization, but that it was very pronounced between 500 and 650 deg. C. Stead has also expressed the belief that alpha iron can combine with carbon to form Fe_3C by heating it in carbon monoxide at 600 deg. C. It is interesting to note the marked stability of the compound Fe_3C in its crystallized condition, compared to the readiness with which it dissociates when in solution in gamma iron above the critical range. Consider, for instance, the ease with which the carbide in white cast iron dissociates on annealing during the manufacture of malleable castings (Chapter XXIII).

Normal and Abnormal Steels. — The occurrence of "soft spots" in hardening case-hardened articles is a frequent occurrence and is a cause of considerable annoyance and loss. These soft spots are generally of a troostitic nature. Extensive investigations have been carried on, partly under the supervision of the Bureau of Standards and largely by E. W. Ehn, and jointly by Ehn and H. W. McQuaid, with a view to discovering the cause of these soft spots, and if possible the means of preventing their occurrence. Steels which, after case hardening, develop soft spots in quenching have been called "abnormal," and those in which soft spots do not occur,

"normal." Conclusions have been reached that the presence of oxygen in the steel resulting from improper deoxidation is the chief cause of abnormality. To quote:

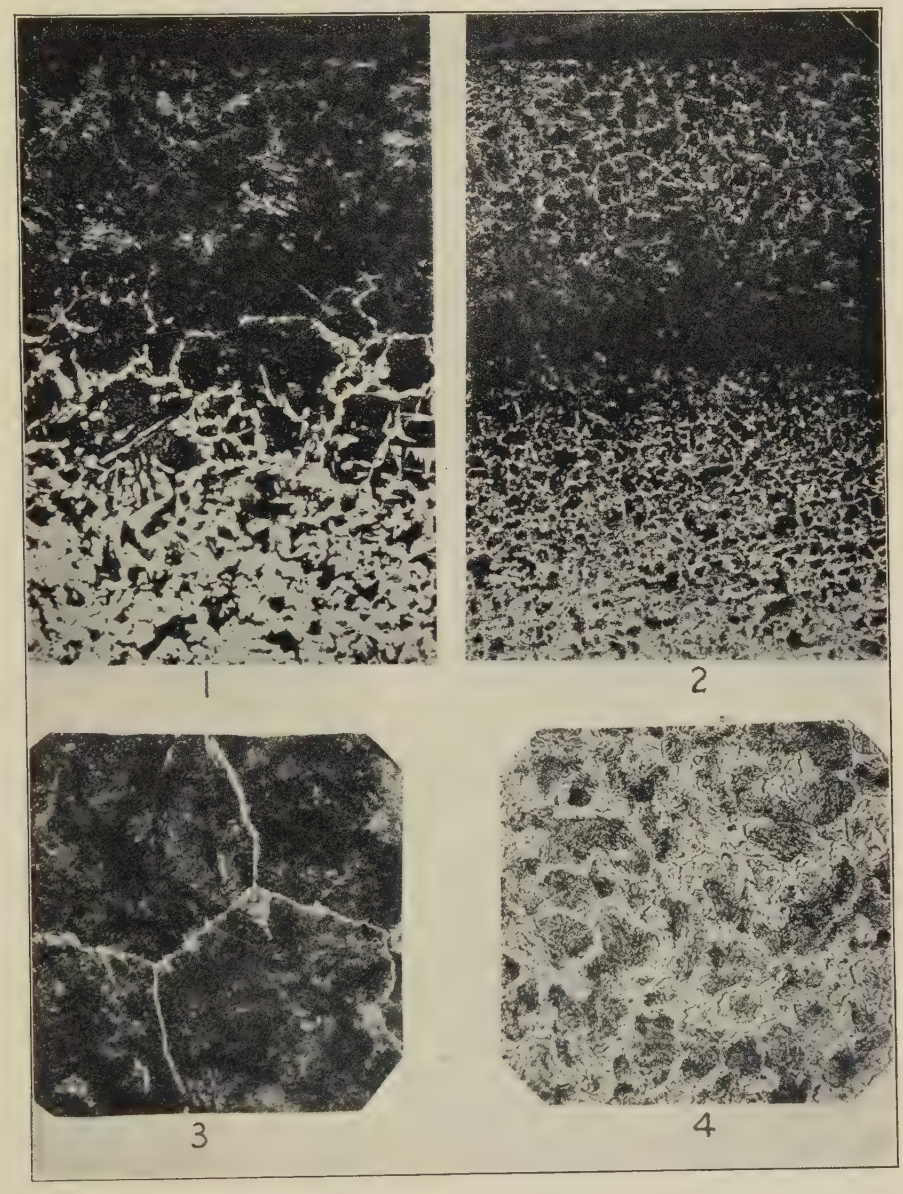


Fig. 275. Fig. 276.

No. 1. Case of normal steel. Magnified 50 diameters. Will give a martensitic case in hardening.

No. 2. Case of abnormal steel. Magnified 50 diameters. Will give soft troostitic spots in hardening.

No. 3. Hyper-eutectoid zone of normal steel. Magnified 200 diameters.

No. 4. Hyper-eutectoid zone of abnormal steel. Magnified 200 diameters. (E. W. Ehn.)

"Steels made with the use of different deoxidizers gave the following results:

"(*a*) All the 'killed' steels, whether deoxidized with silicon, titanium, or zirconium were normal.

"(*b*) The effervescing steels killed in the mold with aluminum were generally abnormal."

Characteristic differences between the microstructure of normal and abnormal steels are shown in Figures 275 and 276.

CHAPTER XIX

ALLOY STEELS

GENERAL CONSIDERATIONS

The steels so far considered in these chapters are the ordinary steels of commerce, at present often called "carbon" steels to distinguish them from the "special" or "alloy" steels of relatively recent origin but of rapidly growing importance. By alloy steels is meant those steels which owe their properties in a marked degree to the presence of one or more special elements, whereas the properties of carbon steels depend chiefly, if not exclusively, for like treatment, upon the proportion of carbon present. It will be obvious that two or even three or four special elements may be introduced with a view of imparting to the steel the beneficial influence of each. Hence, for instance, the value of nickel-chromium steel, chromium-vanadium steel, chromium-tungsten-vanadium steel, etc. Alloy steels containing but one special element are commonly called "ternary" steels, being considered to be made up of three constituents, namely iron, carbon, and the special element, while steels containing two special elements are called "quaternary" steels because of the presence of four constituents: iron, carbon, and the two special elements. These two classes of special steels will be considered separately.

Special Elements. — The so-called special elements used for the manufacture of "special" or alloy steels include manganese, nickel, chromium, tungsten, vanadium, silicon, molybdenum, copper, titanium, cobalt, aluminum, and zirconium.

Condition of Special Elements. — The special elements may be divided into (1) those like nickel, copper, and silicon which do not combine with carbon to form carbides, and (2) those like manganese, chromium, tungsten, vanadium, molybdenum which do form carbides.

Nickel and copper, and also silicon, as the silicide FeSi, are dissolved in gamma iron at a high temperature and retained in solid solution in ferrite at room temperature even after slow cooling.

The carbides of the elements mentioned above may be wholly or partly dissolved in gamma iron at a high temperature, but they separate as free carbides on slow cooling.

Influence of Special Elements. — Speaking broadly, those elements which, like nickel and copper, are retained in solid solution, even after slow cooling, should increase the strength, elastic limit, and hardness of the alloy while decreasing its ductility. In the case of nickel, and, according to some, with moderate amounts of copper also, the decrease of ductility accompanying increased strength and hardness is relatively very slight, hence the importance of nickel steel.

In regard to those elements forming carbides which separate on slow cooling (the carbide steels of Guillet) it should be borne in mind, for reasons made clear later,

that it is seldom if ever desired to use these alloys in that condition, that is when the special elements exist as free carbides, because of their brittleness and for other reasons. The value of these so-called carbide steels will greatly depend (1) upon the readiness with which the carbides can be absorbed at a high temperature, (2) the readiness with which the carbides can be retained in solid solution on cooling at a suitable speed, and (3) their resistance to tempering after absorption of the carbides

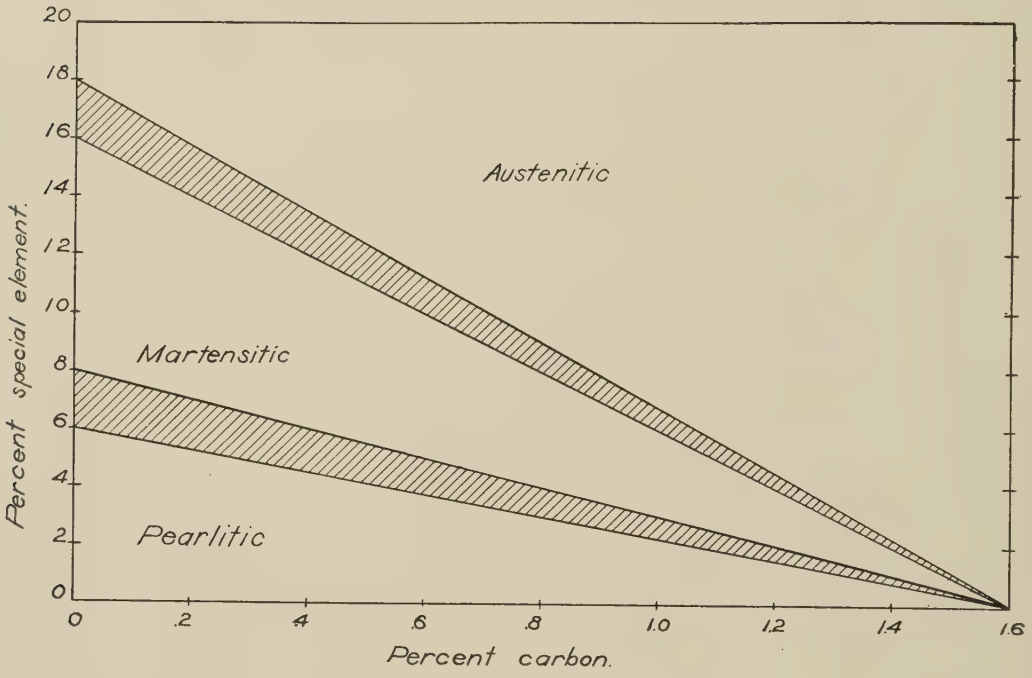


Fig. 277. — Constitutional diagram of alloy steels.

Behavior of Carbides. — Many of the special elements added to steel enter into chemical combination with carbon (1) forming independent carbides, which may be represented by the general formula E_xC_y, in which E stands for the special element, (2) isomorphous mixtures with the carbide of iron, E_xC_y, Fe_3C, or (3) double carbides, $m\ E_xC_y \cdot n\ Fe_3C$.

At a sufficiently high temperature these carbides are dissolved in gamma iron and may be retained at room temperature, in solid solution, partly at least, (1) in gamma iron, or (2) in alpha iron in accordance with the percentage of carbon and of the special element present, with the temperature from which the steel cools and with the rate of cooling. In the presence of a relatively small percentage of the special element the carbides may be completely rejected on slow cooling, being then embedded in a pearlitic matrix. If the carbides are retained in solid solution in gamma iron, it implies that the steel remains untransformed, namely austenitic; if retained in solid solution in alpha iron, it implies that the steel is partially transformed, the iron having undergone its allotropic transformation and the martensitic condition produced. This behavior of the carbides accounts for the treatment and properties of this class of alloy steels.

Ternary Steels. — We are indebted to Guillet for a brilliantly conceived and

vigorously developed theory of the ternary steels. Too rigorous an application of the theory, however, should not be insisted upon, for there are some facts not yet satisfactorily explained by it. Its use, nevertheless, will be found an invaluable guide in directing researches dealing with the manufacture and the application of these steels.

Guillet's theory of the structure and properties of an important class of ternary steels may be briefly formulated by a few propositions. It is also represented graphically in Figure 277, where arbitrary percentages of carbon and of the special element have been selected.

(1) On the introduction of a special element in carbon steel the latter remains at first pearlitic, but as the proportion of the special element increases, the carbon remaining constant, it becomes first martensitic and then austenitic (polyhedral), as shown graphically in Figure 277, and sometimes cementitic (carbide steel),[1] as later explained.

(2) By increasing the amount of carbon present in a special steel, the proportion of the special element being kept constant, it is generally converted from a pearlitic into a martensitic condition or, if already martensitic, into an austenitic condition.

(3) The greater the amount of carbon the smaller the proportion of the special element needed to cause a structural transformation, as for instance pearlite into martensite or martensite into austenite. This is indicated in Figure 277.

(4) The greater the amount of the special element the smaller the proportion of carbon needed to cause a structural transformation. This is also shown in Figure 277.

(5) No very sharp lines of demarcation are observed between the different types of structures mentioned in the preceding propositions, relatively wide ranges of composition existing, on the contrary, in which the steel may be partly pearlitic and partly martensitic or partly martensitic and partly austenitic, etc. These transition ranges are indicated by shaded areas in the diagram of Figure 277. Greater refinement in the construction of this diagram would undoubtedly lead to the introduction of a troostitic zone between the pearlite and martensite areas and possibly also of a sorbitic zone between pearlite and troostite.

To sum up, constituents may be formed during the *slow cooling* of many alloy steels which in carbon steels can only be produced by very rapid cooling through the critical range. Carbon steels, moreover, even after very rapid cooling, cannot be retained wholly in an austenitic condition, while several special steels remain austenitic after slow cooling. It is evident from the above and from the diagram that in order to produce a certain structure, (1) the proportion of carbon may be kept constant while the proportion of the special element is increased until the desired structure is obtained, or (2) the proportion of the special element may be kept constant and the proportion of carbon increased, or (3) both the proportion of carbon and of the special element may be increased, when the desired structure will be obtained more quickly.

The usefulness of Guillet's diagram is obvious. Should we desire, for instance, to know the kind of structure, and therefore the physical properties, of a steel contain-

[1] Guillet uses the term "polyhedral" to designate an austenitic structure and "carbide" steel (*acier à carbure*) to indicate the presence of cementite (generally in special steels a double carbide of iron and the special element). It seems to the author that the terms austenitic and cementitic are preferable because they suggest unmistakably the nature of the constituents. Austenitic steels are not the only ones exhibiting a polyhedral structure; ferritic (low carbon) steels, for instance, are also polyhedral.

ing 0.60 per cent carbon and 8 per cent of the special element, the diagram shows that such composition falls within the martensitic range. Likewise a steel containing 1 per cent carbon and 15 per cent of the special element would be austenitic according to the diagram. Or one may wish to know what proportion of the special element should be added to a carbon steel containing, say, 0.5 per cent carbon, to make it martensitic; the diagram shows that 7 per cent will be needed. Again, having an austenitic steel containing 10 per cent of the special element it may be desired to know the minimum amount of carbon that may be present without causing the

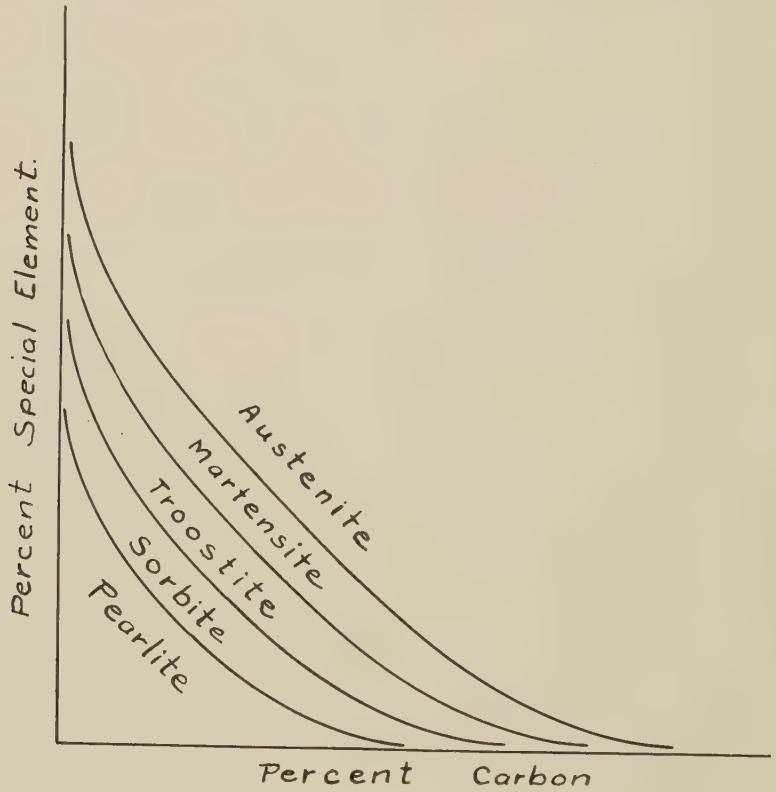


Fig. 278. — Constitutional diagram modified.

steel to become martensitic; the diagram shows 0.80 per cent of carbon to be the smallest proportion of carbon permissible.

The construction of such diagrams requires the preparation of a number of alloys varying in their contents of carbon and of the special element, their microscopical examination, and the plotting of their structure.

It is quite essential to know the rate of cooling adopted in the construction of the diagram, i.e. whether the samples were cooled in air or more slowly in the furnace, for it is evident that their structure may be deeply affected by thus varying the speed at which they cool. Some special steels, for instance, may be pearlitic when cooled very slowly in the furnace, martensitic when cooled in air, and austenitic after water quenching.

It may be assumed that the diagram of Figure 277 represents the structure of the steels after air cooling.

On further reflection it will be evident that in Guillet's diagrams the diagonal lines of demarcation between the various types of structure should not intersect the axes but should be asymptotic to those axes.

With more than 1.60 per cent carbon and in the absence of the special element, the steel cannot be austenitic, as the diagrams would indicate, nor can it be austenitic with more than 18 per cent of the special element unless carbon be present. It is evident that as the percentage of carbon increases in the absence of the special element, or as the percentage of the special element increases in the absence of carbon, the

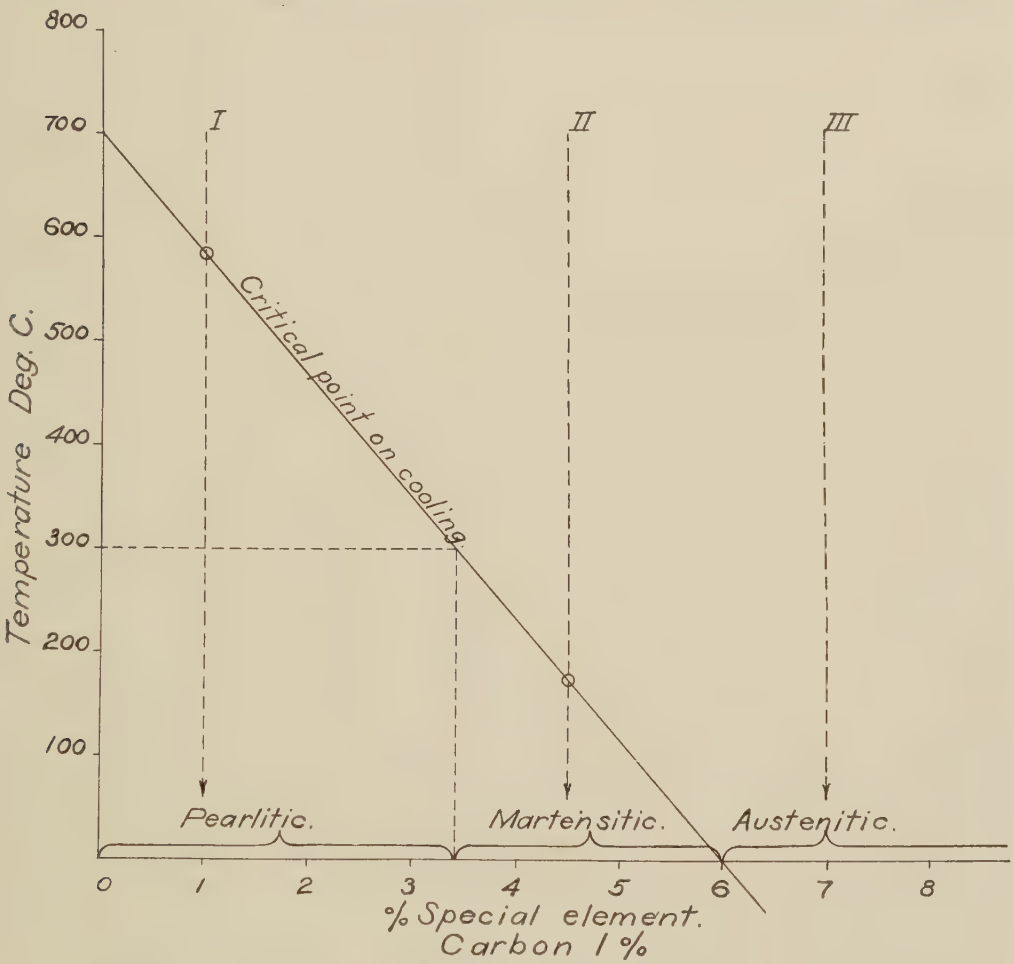


Fig. 279. — Influence of special element on the position of the critical point.

tendency to assume an austenitic structure increases but will never actually be reached. These views are expressed diagrammatically in Figure 278. Additional lines have been introduced in order to provide for the possible formation of troostite, and even of sorbite, as it seems should be done. It may be assumed that this diagram refers to air cooling. A slower cooling would cause all the lines to spread apart, while faster cooling would bring them closer together. To include the action of the rate of cooling would require a third dimension.

Influence of the Special Element upon the Location of the Critical Range. — The production of martensitic and austenitic structures on slow cooling is due to the fact that some special element lowers the position of the critical point to a temperature so low (1) as to permit only a partial transformation, namely, of austenite into martensite, the steel being too rigid to allow a more complete transformation, or (2) as to prevent even a slight transformation, the steel in that case remaining austenitic. This influence of the special element in lowering the position of the critical range is depicted in Figure 279, in which it is assumed that the proportion of carbon remains constant. It has been further arbitrarily assumed in this diagram that the critical point was progressively and uniformly lowered from 700 to 0 deg. C., as the proportion of the special element increased from 0 to 6 per cent. From many observations it appears (1) that as long as the critical point remains above 300 deg. C. the steel becomes pearlitic or sorbitic, or if the point is lowered to some 600 deg. C., troostitic on slow cooling, (2) that when the critical point is lowered below 300 deg. it becomes martensitic, the rigidity of the metal preventing further transformation, and (3) that when the critical point is lowered to atmospheric temperature or below it the metal remains untransformed, that is austenitic. These inferences are offered here because of their apparent usefulness and suggestiveness, but the author realizes that the lines indicating the relation between the position of the critical points and the corresponding structures cannot be sharply drawn, for they are likely to shift according to the nature of the special element, the rate of cooling, etc.

To make the meaning of the diagram of Figure 279 clear let us consider three steels: I, II, and III, all containing 1 per cent of carbon, but respectively 1, 4.50, and 7 per cent of the special element. As steel I cools it undergoes its transformation above 600 deg. At that temperature the metal is so plastic that the transformation of austenite into pearlite readily takes place; the steel becomes pearlitic. With 2 per cent of carbon the transformation would take place below 600 deg. At this temperature austenite may transform into troostite, but the metal is now too rigid to permit further transformations, the steel remaining chiefly troostitic. Steel II transforms below 300 deg. C., and consequently remains martensitic. Steels which remain martensitic after slow (air) cooling are said to be "self-hardening." In the case of steel III, since its critical point is lowered below atmospheric temperature it necessarily remains austenitic. Since austenitic special steels have their points of transformation situated below atmospheric temperature, it should be possible through cooling to a sufficiently low temperature, as for instance by immersion in liquid air, to cause at least their partial transformation, that is, they should become martensitic after such treatment, and this indeed is precisely what happens in some cases. The transformation of austenite into martensite takes place with increased volume and the steel from non-magnetic becomes magnetic.

In the presence of a special element lowering the critical points the influence of carbon is cumulative, i.e. the greater the proportion of carbon the more marked the action of the special element. An attempt has been made in Figure 280 to show this graphically. The diagram indicates the position of the critical point corresponding to any combination of carbon content between 0.25 and 1.50 and of the special element between 0 and 12 per cent. If the point is above 300 deg. we may assume that the steel is pearlitic, sorbitic, or troostitic, if below 300 that it is martensitic, if at or below atmospheric temperature that it is austenitic. In this illustration arbitrary values have been given to the combined influence of various proportions of carbon

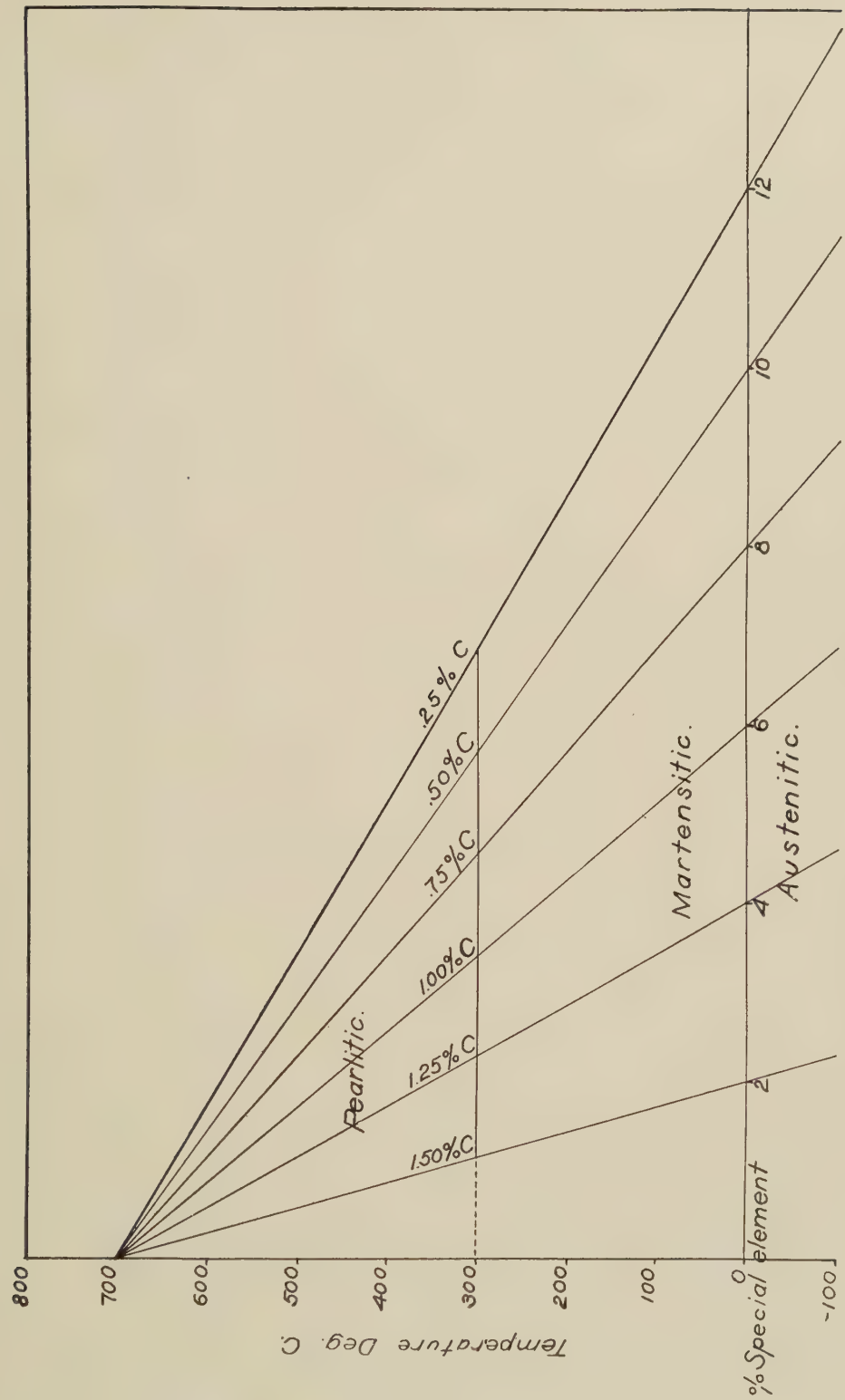


Fig. 280. — Influence of carbon and special element on the position of the critical point.

and of the special element upon the position of the critical points. The diagram shows, for instance, that while with 0.50 per cent carbon 10 per cent of the special element is required to lower the critical points to 0 deg. C., if the steel contains 1.25 per cent carbon, 4 per cent of the special element suffices. The production of pearlitic, martensitic, and austenitic structures according to the position of the critical point has also been indicated. A diagram of this kind may be even more useful than Guillet's, for while giving the same kind of information as his, it shows in addition (1) the relation between the composition of the special steel and the position of the critical point, and (2) the influence of the position of the critical point upon the structure. Its construction calls for many determinations of the position of the critical point in steels of varying composition and for the microscopical examination of the corresponding structures. It is of course quite likely that as experimentally constructed it would consist of more or less smooth curves rather than of straight lines.

It will soon be shown that the influence of special elements in lowering the critical points varies greatly, from which it follows that some elements cause the production of martensitic and austenitic steels much more readily than others. Indeed some elements never cause a sufficient depression of the critical points to yield austenitic or even martensitic steels. Some elements even actually raise the location of the critical points.

Although a large amount of experimental work has been done to ascertain the exact influence of the various elements on the position of the thermal critical points of iron-carbon alloys the available data is not so complete and so accurate as it should be. Some elements may cause all critical points to be lowered or to be raised, some may result in some points being lowered and other points raised, others still may cause the complete disappearance of some or of all points.

Chromium, tungsten, molybdenum, and silicon have a tendency to raise the critical points, at least those on heating. Nickel, manganese, and copper depress those points.

From the action of these elements on the critical points, it is possible to predict with fair accuracy the structure and hence the properties of these alloy steels after various heat treatments.

Self-Hardening Steel. — The term self-hardening is generally applied to steels which become hard (martensitic) on cooling in air from a sufficiently high temperature; they are also properly called air-hardening steels. Some alloy steels, however, become hard on slow cooling in the furnace. They might be called furnace-hardening steels. Obviously they are also air-hardening, while air-hardening steels are not necessarily furnace hardening. We could in the same way speak of air-hardening, oil-hardening, and water-hardening steels to distinguish between those hardening in water but not in oil and between those hardening in oil but not in air. Starting, for instance, with moderate amounts of nickel and chromium, the steel, like carbon steel, must be quenched to be hardened. Water quenching may first be required, and then oil quenching may suffice. With gradual increase of nickel and chromium, they become air hardening and then furnace hardening until the transformation is prevented altogether, when they remain austenitic — first after quenching, and then after air cooling, and then even after furnace cooling.

Chrome-nickel steels, for instance, and other alloy steels might be described as (1) water-hardening, (2) oil-hardening, (3) air-hardening, (4) furnace-hardening, (5) water-austenitic, (6) oil-austenitic, (7) air-austenitic, and (8) furnace-austenitic

steels in accordance with the conditions resulting from the treatments indicated, which in turn depends upon the percentages of carbon, nickel, and chromium, the steels passing gradually from class (1) to class (8) as the percentages of these three constituents increase.

More recent investigations of the action of some elements in depressing the Ar_1 point have revealed the fact that it is very similar to the action of the cooling velocity on carbon steels, as will readily be seen by comparing Figure 281 with Figure 191, Chapter XIV. As the percentage of the special element increases, the Ar_1 point is

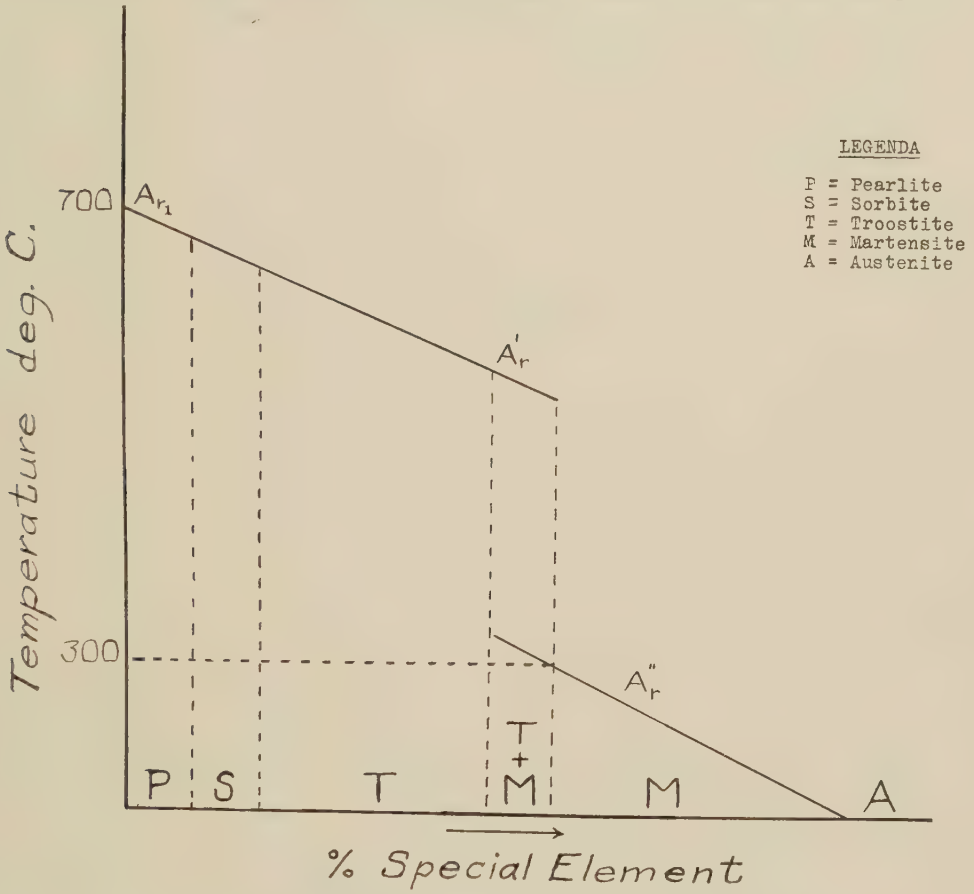


Fig. 281. — Percentage of special element vs. position of Ar_1.

at first gradually lowered, and pearlite, sorbite, or troostite is formed, until a certain percentage is reached which may be called the critical percentage, recalling the critical speed of quenching, and which causes the sudden lowering of the Ar_1 point to some 300 deg. C., accompanied by the formation of martensite. Further addition of the special element may result in the Ar_1 point being depressed below room temperature and in the steel remaining untransformed, that is austenitic.

The cumulative action of the percentage of carbon, the percentage of the special element, the cooling velocity, and the quenching temperature in lowering the critical point Ar_1, resulting in partial transformation of austenite and finally in preventing its transformation altogether, is graphically illustrated in Figure 281a.

T^{max}. — The elements such as chromium, tungsten, molybdenum, and silicon, which have a tendency to raise the critical points, generally intensify the action of T^{max}, that is of the temperature from which cooling begins (Chapter VII). Some chromium-tungsten steels, for instance, pearlitic on air cooling from a moderately high temperature, become martensitic, or even remain austenitic (untransformed) if air cooled from a very high temperature. It is the treatment applied to high-speed steel.

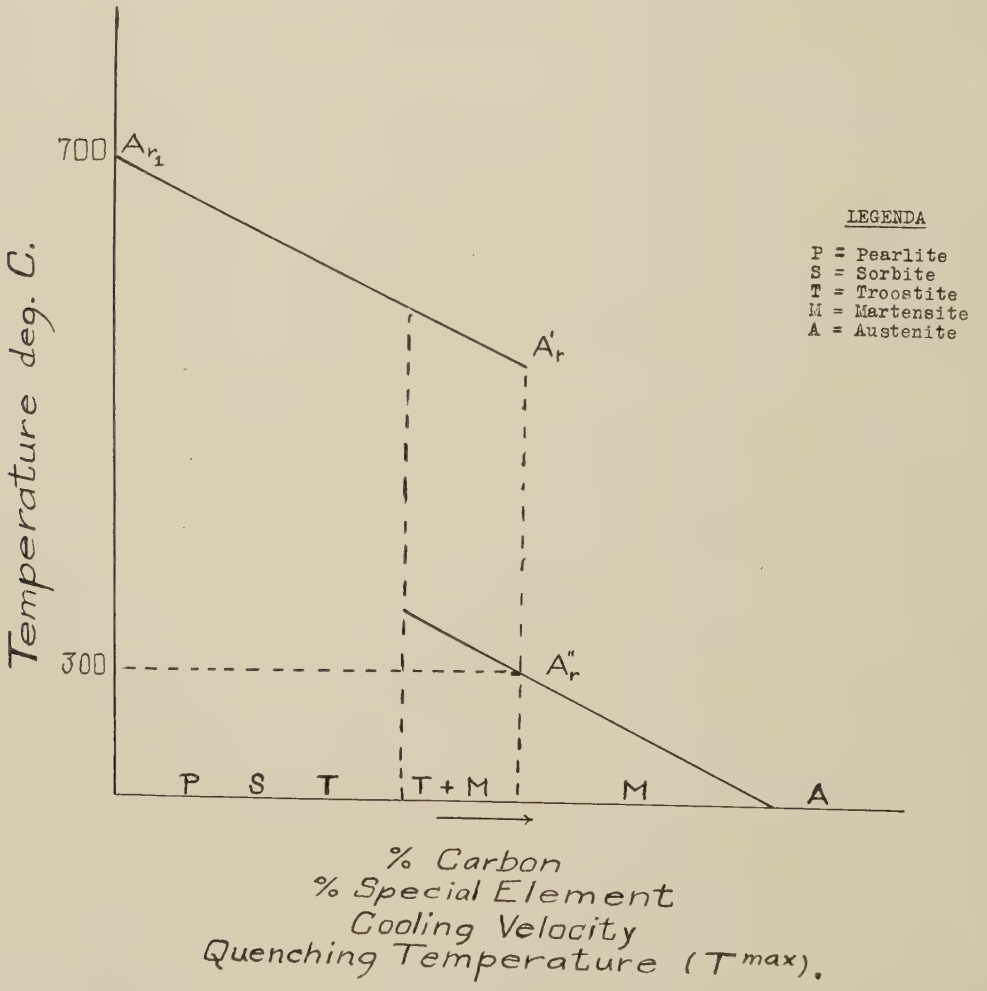


Fig. 281a.

Hysteresis. — It is frequently observed that whether a special element lowers or raises a critical point, it often increases hysteresis, that is, the gap between the Ac and Ar points. When that gap is considerable the steel is said to be irreversible, while if moderate, the steel is described as reversible, meaning by that that the reverse transformation readily takes place at nearly the same temperature. Manganese and nickel lower decidedly the critical points, while chromium, tungsten, molybdenum, and silicon raise them. These elements also increase hysteresis. It has been attempted to show this diagrammatically in Figure 282.

As stated by Portevin, elements such as manganese, nickel, chromium, tungsten, molybdenum, vanadium, etc., increase the thermal hysteresis Ac-Ar; but some of them, nickel and manganese, lower Ac, while others — chromium, tungsten, molybdenum, silicon — have a tendency to raise it. Hence, with nickel and manganese steels the hardening temperature is lowered, while it is increased with chromium, tungsten, molybdenum, and silicon.

Because of increased hysteresis a special element may raise the point Ac while lowering the Ar point. Hence to harden, a higher temperature may be required, while a slower cooling may suffice.

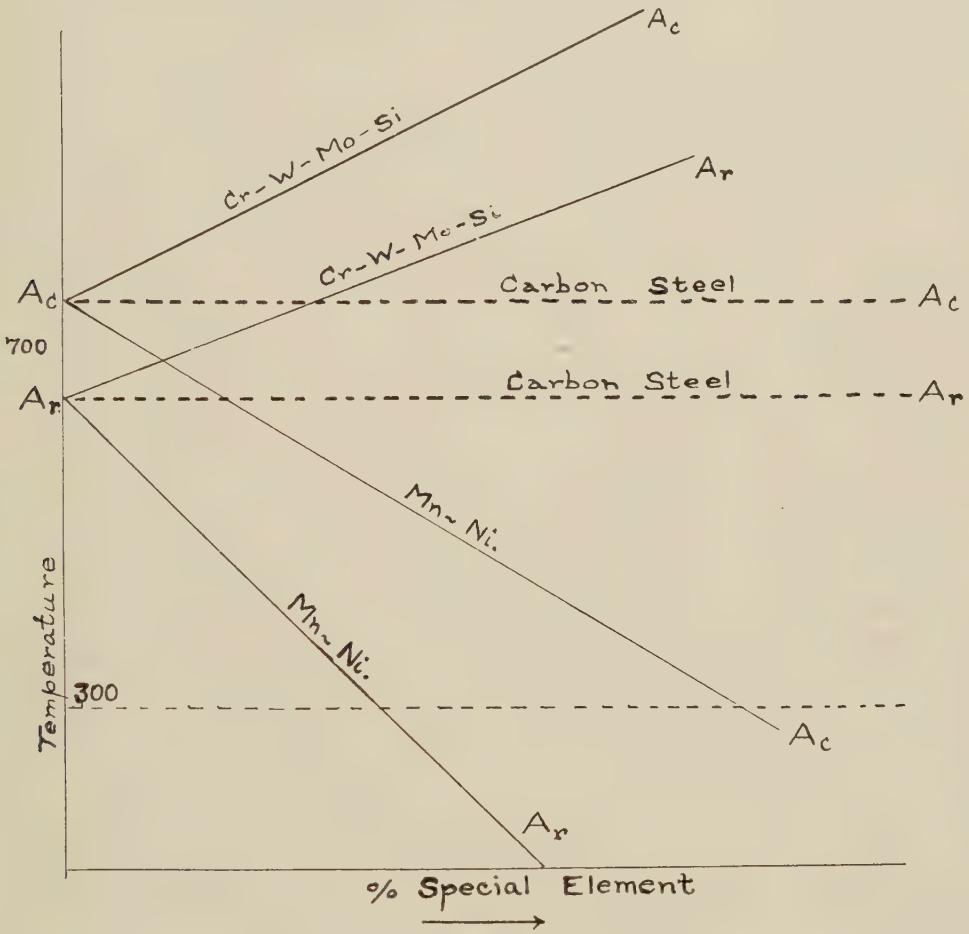


Fig. 282. — Hysteresis vs. special element.

Special Elements vs. Eutectoid Point. — The special elements of alloy steels generally lower the percentage of carbon required to produce eutectoid steel, that is to cause the complete disappearance of free ferrite in the structure. To express it differently, their action is to shift the eutectoid point to the left in the iron-carbon equilibrium diagram (Chapter XXV). This important influence of special elements should be remembered, as it helps us in understanding the marked difference existing between carbon steels and alloy steels. For like percentages of carbon the carbon steel may be hypo-eutectoid, the alloy steel, hyper-eutectoid.

Classification of Alloy Steels. — To generalize, alloy steels may be divided into (A) those which become pearlitic or sorbitic on air cooling, (B) those which become troostitic or martensitic after air cooling, (C) those which remain untransformed, that is austenitic, and (D) those containing a substantial amount of free carbides. The steels of group A are chiefly used for structural and constructional purposes and may be heat treated like carbon steels. Indeed, their superiority is to a great extent manifest only after heat treatment. They are often more sensitive to heat treatment and yield higher tensile strength, elastic limit, and hardness combined with ductility. They are also more resistant to impace and to fatigue stresses, and also to wear. They are more responsive to the action of T^{max}, some of them becoming air hardening if cooled from a high enough temperature. Their microstructure is as a rule finer and they require less carbon to be of eutectoid composition. Some of them possess greater hardening power and acquire greater depth of hardness after quenching.

The steels of group B are air hardening and do not therefore require quenching. The danger of the steel cracking in the quenching operation is consequently eliminated. In their martensitic condition they are, moreover, more stable than quenched carbon steels, i.e. they may be heated to higher temperatures without losing their hardness, hence permit more rapid cutting when used as tools.

The steels of group C are very resistant to abrasion although very tough, at least after suitable heat treatment. They are used, therefore, for parts subjected to very severe abrasive wear. Some of them become martensitic, hence very hard on prolonged heating, by friction or otherwise, to a sufficiently high temperature. The important alloy steel known as Hadfield manganese steel belongs to this class.

The steels of group D are generally subjected to such heat treatment as to cause most if not all the free carbides to be absorbed and retained in solution at room temperature, the steels assuming the austenitic or martensitic condition.

Pearlitic Steels. — The pearlitic steels, as we have seen, are those which generally contain but a relatively small amount of the special element, although in case of steel very low in carbon the proportion of the special element may be quite large. In these steels the special element may (1) be dissolved in the ferrite, forming with it a solid solution, (2) be combined with carbon in cementite as a double carbide of iron and the special element, or (3) be partly dissolved in ferrite and partly combined with carbon.

According to Guillet, nickel and silicon, for instance, are entirely dissolved in ferrite, while manganese, chromium, tungsten, vanadium, and molybdenum are partly held in solution by ferrite and partly present in cementite as double carbides. Such terms as nickel-ferrite, silico-ferrite, mangano-ferrite, etc., have been suggested to designate ferrite holding in solution large proportions of nickel, silicon, manganese, etc., respectively.

The structure of pearlitic alloy steels is generally quite similar to that of pearlitic carbon steels, although the pearlite particles of special steels frequently are more angular than those of carbon steel, often exhibiting many straight sides and sharp corners, whereas the pearlite particles of carbon steel are more rounded. The lamination of pearlite is also often more minute in special steels, while for same carbon content pearlite occupies a larger bulk owing to the influence of the special element on the eutectoid point already noted. From their similarity of structure, it might reasonably be inferred that pearlitic special steels should not differ much in physical properties from ordinary carbon steels. As a matter of fact, however, pearlitic special

steels are often greatly superior to carbon steels generally because they possess in a much greater degree that desirable combination of properties, strength, or rather high elastic limit, and ductility. They are also frequently harder for like ductility, and therefore better adapted to resist wear. Finally their ability to resist shocks is often markedly superior to that of carbon steels. Their uses make for greater efficiency and their greater strength permits an often welcome reduction in bulk and weight of certain parts of machinery. This greater strength and stiffness of special pearlitic steels may be due to the special element dissolving, in part at least, in the ferrite, thereby increasing its strength, elastic limit, and hardness, a stronger and harder ferrite resulting in turn in a stronger and harder pearlite. The superior physical qualities of these steels may also be due, at least partly, to a finer, closer ferrite-cementite aggregate.

The percentages of the special elements which may be present in steel as the carbon increases from 0.10 to 1.00 per cent and still retains it in a pearlitic condition after air or furnace cooling, are approximately as indicated in the following table:

Carbon	0.10	to 1	per	cent
Nickel	8	" 4	"	"
Chromium	7	" 3	"	"
Nickel and chromium	8	" 4	"	"
Manganese	3	" 2	"	"
Molybdenum	2	" 0.75	"	"
Vanadium	1	" 0.75	"	"
Tungsten	9	" 4	"	"

In a steel containing 0.10 per cent carbon, as much as 8 per cent nickel may be present, while with 1 per cent carbon not over 4 per cent. Proportions of the special elements in excess of those indicated will cause the nickel, chromium, and manganese steels to become troostitic or martensitic, that is air hardening, while free carbides will be present in the molybdenum, tungsten, and vanadium steels.

Martensitic Steels. — For the same carbon content martensitic steel contains necessarily more of the special element than pearlitic steels, while for a given proportion of the special element they must contain more carbon; they generally contain both more carbon and more of the special element than pearlitic steels. As already stated the influence of some special elements in lowering the critical points is not sufficiently pronounced to result in the formation of martensite on slow cooling. Indeed some elements raise the position of the critical points, in which case pearlitic steel must necessarily always be formed on slow cooling.

The properties of martensitic special steels are not unlike the properties of martensitic carbon steels, that is of hardened carbon steel. These steels are hard and brittle and unforgeable in the cold. Their uses are very limited, chiefly because of their brittleness and of the difficulty of machining them. While resembling hardened carbon steels they are quite stable above atmospheric temperature, being little affected by tempering, i.e. by reheating to 200 or 300 deg. C. This property suggests one important application at least of martensitic special steels later to be considered, namely, their use for the manufacture of cutting tools, their greater stability permitting the tools to be heated to a higher temperature, i.e. the cutting being performed at greater speed without breaking down through excessive tempering.

The martensite of special steels is generally considered to be, like the martensite of carbon steels, chiefly a solid solution in alpha iron of the carbide Fe_3C, or more

often of a double carbide of iron and of the special element, the magnetism of the metal being due to the presence of some alpha iron.

Austenitic (Polyhedral) Steels. — For a given carbon content austenitic steels necessarily contain more of the special element than martensitic steels, while for a given proportion of the special element they are necessarily more highly carburized. Austenitic steels generally contain both more carbon and more of the special element than martensitic steels. Their properties are, as might be expected, similar to those of austenitic carbon steels, that is of high carbon steels cooled extremely quickly from a very high temperature. Austenitic steels are moderately tenacious but very ductile; they have a low elastic limit but possess a remarkable power of resisting wear by abrasion as well as rupture by shocks. Their mineralogical hardness, however, is generally inferior to that of martensitic steels.

Unlike quenched austenitic carbon steel these special steels are stable at all temperatures below their point of solidification and are not therefore greatly affected by heat treatment unless of a protracted nature. They should be free, however, from separated carbides. If not they should be heated to a high temperature so as to cause the solution of these carbides, and then quenched to prevent their separating again.

The austenite of special steels undoubtedly consists of a solid solution in gamma iron of carbon and of the special element, probably of a double carbide. Because of the absence of alpha iron austenitic steels are non-magnetic.

Hadfield austenitic manganese steel finds extremely useful application for parts of machinery and the like, and for rails subjected to very severe wear by abrasion and to shocks.

Cementitic (Carbide) Steels. — Some special elements on being introduced in increasing proportions fail to convert the metal into austenite, free particles of a double carbide of iron and the special element being formed instead and embedded in a martensitic, troostitic, sorbitic, or pearlitic matrix. Guillet calls these "carbide" steels. Such elements as chromium, tungsten, molybdenum, and vanadium when present in sufficient quantity produce cementitic steels. The most valuable property of these steels is their power, when the carbides are embedded or rather dissolved in a martensitic or austenitic matrix, of retaining their hardness when heated to such temperature as would readily cause the softening of hardened carbon steel, thus permitting their use in the shape of tools at such speed as to cause their cutting edges to become visibly hot. This phenomenon will be further explained when describing self-hardening and high-speed steels.

Treatments of Special Steels. — Special steels are subjected to the same treatments as carbon steels, i.e. to hot and cold working, annealing, hardening, and tempering, and to case hardening. Since the special elements, however, often have a marked influence on the position of the critical points it is obvious that the temperatures indicated as the most suitable ones for the annealing and hardening of carbon steels may not be satisfactory in the case of special steels. The position of the critical points should in every case be determined and the heat treatments conducted accordingly. Greater care is also frequently needed in the forging of special steels, many of them not being quite so malleable as carbon steels. Finally some of the special elements promote the absorption of carbon by iron below its solidification point while others oppose it, and these influences must be considered in case hardening special steels. The treatment of special steels will be considered further in the next chapter in connection with the description of some of the most important commercial types.

Treatment of Pearlitic Steels. — Pearlitic special steels may, like carbon steels, be subjected to annealing, hardening, tempering, and case hardening. Their critical points, however, being generally lower, the proper temperatures for these operations are likewise lower. They should be determined for each steel. According to Guillet, however, the steel should be heated quite a little above its critical range because in the case of the pearlite of special steels its transformation into a solid solution does not take place so readily. The steel should then be cooled to near its critical range before quenching. Guillet writes that pearlitic special steels may be divided into (1) those that are not very sensitive to annealing, namely nickel and silicon steels, and (2) those that are very sensitive to annealing, namely manganese, chrome, vanadium, tungsten, and molybdenum steels. It should be noted that in the first group the special elements are supposed to be entirely dissolved in the iron, while in the second group they are partly dissolved and partly present as carbides. The case hardening of pearlitic special steels may result in the production of martensitic or even austenitic cases without the necessity of rapid cooling from above the critical range. This will be readily understood by referring to Figure 277, where it will be seen that by keeping the proportion of the special element constant and increasing the carbon, the steel may be converted from a pearlitic to a martensitic and even to an austenitic condition. The nearer the steel to the boundary between the pearlitic and martensitic zones the more readily, of course, will it become martensitic on case hardening because the smaller the amount of carbon needed to produce that transformation. This possibility of producing steel objects with a pearlitic soft core and a hard martensitic shell without quenching from a high temperature and therefore without exposing the objects to the dangers of the quenching bath does not seem to have received the attention it deserves, for it suggests important practical applications; and likewise the production of a soft pearlitic core surrounded by a hard martensitic steel, itself surrounded by a tough austenitic steel. It points at least to the manufacture of pearlitic steel objects which can be readily machined, etc., and as a last treatment made austenitic to a certain depth, being in this way greatly superior to the austenitic steels at present used, which being cast in an austenitic condition can be machined only with very great difficulty.

Treatment of Martensitic Steels. — Unlike martensitic carbon steels, martensitic special steels being quite stable below the critical range of the metal are not readily affected by tempering treatments. It should be borne in mind, however, that some special steels which are martensitic after air cooling may become pearlitic, in part at least, after very slow cooling in the furnace and austenitic or martensito-austenitic after quenching in water. By selecting a special steel of suitable composition, for instance, and allowing it to cool in a furnace it becomes pearlitic and can in consequence be machined; after machining, the finished object may be made martensitic by cooling in air, doing away with the necessity of the quenching bath and its inherent evils. It is evident that for this purpose the composition of the steel should be near the boundary line between the pearlitic and martensitic zones. The author believes that the practical possibilities of this procedure have been overlooked. When working near the pearlito-martensitic boundary line the formation of troostite is of course always likely.

Treatment of Austenitic Steels. — Austenitic special steels are stable, theoretically at least, at all temperatures and should not, therefore, be affected by heat treatment of any kind. Some special steels, however, may require air cooling to be truly

austenitic, in which case very slow cooling in the furnace may result in the production of some martensite or troostite and even of some pearlite, accompanied by the reappearance of magnetism. It also frequently happens that during the relatively slow cooling of austenitic steels some free cementite may be formed, consisting generally of a double carbide of iron and the special element, this setting free of cementite being generally accompanied by a decided decrease of strength and ductility. In order to cause the reabsorption of the separated carbide, heating to a high temperature (1000 deg. C. or higher) is generally required, followed by rapid cooling in water or oil so as to prevent its separating again on cooling. This treatment is sometimes called "water toughening."

Treatment of Cementitic Steels. — Cementitic steels contain many particles of cementite or double carbide embedded in a matrix which may be austenitic, martensitic, troostitic, sorbitic, or pearlitic according to the rate of cooling. It is often desirable to cause the disappearance, in part at least, of these particles while producing a finely martensitic or austenitic structure, and for this purpose heating to a high temperature (1000 deg. C. or more) followed by relatively quick cooling is necessary. Cooling in air is often sufficiently rapid to retain the carbide in solution, as for instance in the case of the high-speed steels soon to be described.

Quaternary Steels. — Quaternary steels like ternary steels may be pearlitic, martensitic, austenitic, or cementitic as well as sorbitic and troostitic. If the two special elements are present in small quantities the steels remain pearlitic. If they contain one or two cementite-forming elements such as chromium, tungsten, molybdenum, etc., they are likely to be cementitic, that is, to contain many particles of a double or triple carbide. These should generally be made to dissolve in the matrix by heating to a high temperature followed by rapid cooling, when a finely martensitic or austenitic structure, quite free from cementite, may be produced, as in the treatment of high-speed steel. If the quaternary steels contain considerable proportions of two special elements capable of forming solid solutions with iron, as for instance nickel and manganese, they are frequently martensitic or austenitic. A large proportion of an element which is partly dissolved in ferrite and partly present in cementite as a double carbide — manganese, for instance — may result in the occurrence of cementite particles embedded in an austenitic matrix.

Brittleness of Some Heat-Treated Special Steels. — A phenomenon frequently described as "blue brittleness" is sometimes observed in alloy steels, and more especially in nickel-chromium steels. When some of these steels are slowly cooled from the drawing temperature after quenching, although their tensile properties may be all that could be desired, they break readily under shock in the Charpy or Izod machines, while the same steels after quenching from the drawing temperature show considerable resistance to rupture and impact. The moral, therefore, is that such steels should be quenched from the drawing temperature.

CHAPTER XX

ALLOY STEELS

CONSTITUTION, PROPERTIES, TREATMENT, AND USES OF THE MOST IMPORTANT TYPES

The present chapter is devoted to a brief consideration of the composition, structure, properties, treatments, and uses of those special steels which have long passed the experimental stage and have been found to be of commercial value, namely, nickel, manganese, tungsten, chromium, vanadium, silicon, molybdenum, chrome-nickel, chrome-vanadium, chrome-tungsten, and chrome-molybdenum steels.

Nickel Steel

Nickel apparently dissolves in all proportions both in gamma and in alpha iron. In the presence of carbon, it remains dissolved in gamma iron above the critical range of the steel, and in alpha ferrite below that range. Some believe that a little

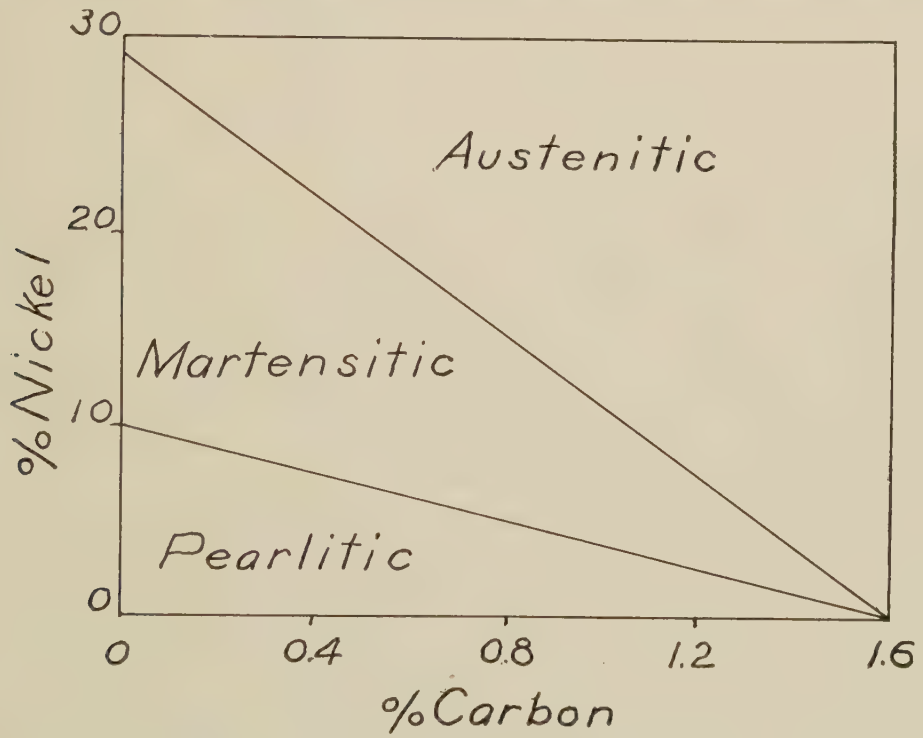


Fig. 283. — Nickel steel. Constitutional diagram. (Guillet.)

nickel is present in the cementite of nickel steel. The constitutional diagram of nickel steel is illustrated in Figure 283 after Guillet. In view of the explanation of such diagrams given in the preceding chapter it will be readily understood. It shows that as the carbon increases from 0 to 1.60 per cent and the nickel from 0 to 30 per cent the metal which at first remains pearlitic becomes martensitic, and finally austenitic. This influence of nickel in preventing partly or wholly the transformation of austenite into pearlite is due to its lowering the critical point of the steel, as fully explained in the last chapter and as illustrated graphically in Figure 284 in the case of iron-nickel alloys containing small proportions of carbon, and in Figure 285,

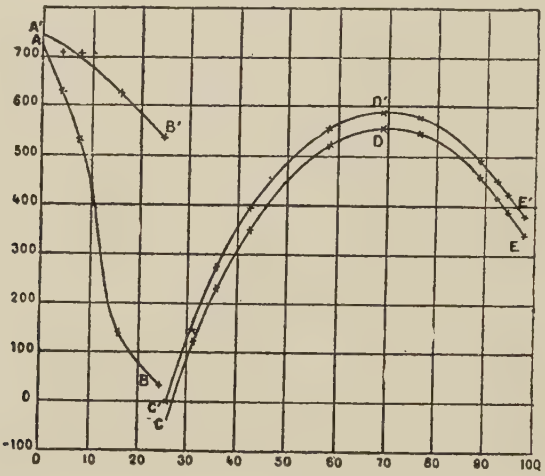


Fig. 284. — Influence of nickel on the critical points of iron. (Osmond.)

according to Dejean, for steel containing 0.20 per cent carbon and from 0 to 30 per cent nickel.

This diagram shows that when the alloy contains less than 10 per cent nickel it transforms at the point Ar_1 with formation of pearlite (or sorbite), and when it contains from 10 to 25 per cent nickel it transforms at the low temperature A″r with formation of martensite. With a greater percentage of nickel, it remains untransformed, that is austenitic. It is probable that in the vicinity of 10 per cent nickel the steel transforms partly at A′r and partly at A″r, and that it contains therefore both troostite and martensite. This action of nickel will be seen to be similar to that of an increasing cooling speed in carbon steel (Chapter XIV, Fig. 191).

It should be remembered that the presence of larger quantities of carbon would intensify the influence of nickel, i.e. would cause the critical points to be further depressed. The diagram (Fig. 284) shows that as the nickel increases from 0 to some 25 per cent both transformations, AB on cooling and $A'B'$ on heating, are depressed, the former, however, much more quickly than the latter, resulting in a rapidly increasing gap between the two transformations. In other words, nickel up to 25 per cent greatly increases the hysteresis. Taking a steel, for instance, with 10 per cent nickel cooling from a high temperature, it remains non-magnetic until a temperature of some 400 deg. C. is reached, when it undergoes its magnetic and other transformations. On reheating this magnetic steel, however, it does not again

lose its magnetism until a temperature of some 675 deg. is attained. Between 400 and 675 deg. this nickel steel will be magnetic, therefore, in case its last transformation resulted from cooling below 400 deg. and it will be non-magnetic if it resulted from heating above 675 degrees. When this hysteresis gap between the transformation is considerable the alloys are said to be irreversible, meaning by that expression that the reverse transformation cannot be produced at or near the same temperature.

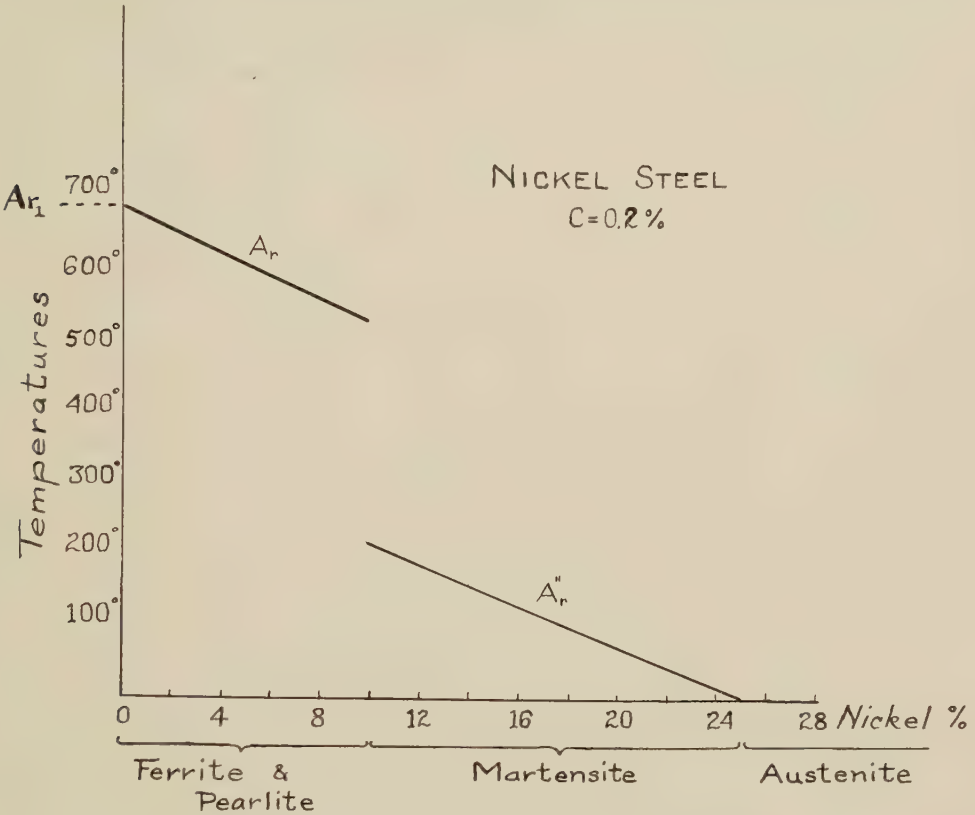


Fig. 285. — Nickel vs. position of Ar_1. (Dejean.)

Nickel steels containing between 5 and 25 per cent nickel are therefore often spoken of as irreversible alloys. It should be noted, that when the nickel content does not exceed some 3 per cent the alloys are really reversible, that is, the gap between the critical transformations on heating and cooling is not excessive. According to Osmond, for instance, with 3.82 per cent nickel the critical point on heating occurs at 710 deg. and on cooling at 628 deg. A gap of 100 degrees might be arbitrarily selected as a line of demarcation between reversible and irreversible alloys. Returning to Figure 284 it will be seen that as the nickel content increases above 25 per cent the transformations become abruptly reversible (the gap between them not exceeding 50 deg.), that their position is now gradually lifted, reaching a maximum for about 70 per cent nickel, and that it is then again lowered. Iron-nickel alloys containing more than 25 per cent nickel are therefore reversible.

The diagram also shows that with some 25 per cent nickel the transformation is lowered below atmospheric temperature, which means that the metal on cooling from

above B' remains non-magnetic at atmospheric temperature and that its iron, therefore, is in the gamma condition and its structure austenitic.

An attempt has been made in Figure 286 to construct a diagram indicating the relation existing between carbon content, nickel content, position of the critical points on cooling, and corresponding types of structures as explained in Chapter XIX.

The action of nickel on the critical point of iron-carbon alloys is also well illustrated, according to Scott, in the diagram of Figure 286a. The steels studied contained 0.40 to 0.50 per cent carbon and increasing amounts of nickel. The diagram recalls the influence of the speed of cooling in quenching carbon steel (Chapter XIV,

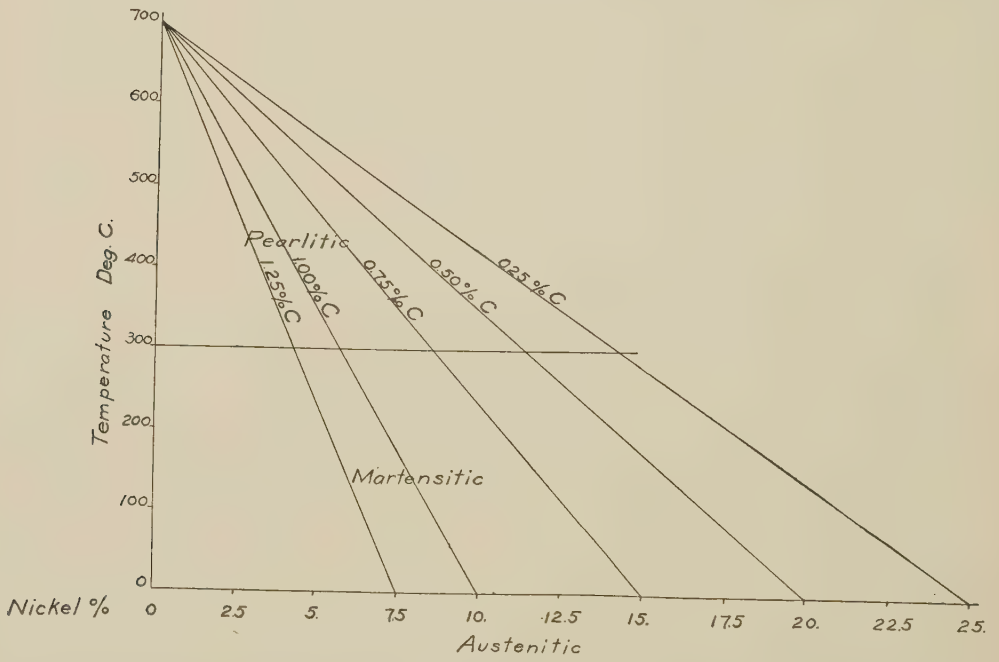


Fig. 286. — Influence of nickel and carbon on the position of the critical point Ar_1 and corresponding types of structure.

Fig. 191). With 1 per cent of nickel Ar_1 and Ac_1 occupy their normal position. Increasing the nickel to 5 per cent results in lowering both Ar_1 and Ac_1, the former, however, more decidedly, which results in increased hysteresis, the steels becoming irreversible. With further increase of nickel, Ar_1 continues to be depressed, while a second point occurs below 200, the two points being now designated respectively as A′r and A″r. We naturally infer that the steel contains now both martensite and troostite. On further addition of nickel the A′r point disappears, the steel undergoing transformation only at A″r, which is further depressed. It should now be fully martensitic. Finally, with a still greater amount of nickel (some 15 per cent or more) the A″r point is lowered below room temperature, the steel remaining untransformed, that is austenitic.

Nickel in common with many other special elements decreases the percentage of carbon required to produce a eutectoid steel. With 4 to 5 per cent nickel, 0.65 per cent carbon suffices.

Nickel probably intensifies dendritic segregation, resulting in pronounced banded structure in forged articles and in directional properties. It is believed to decrease

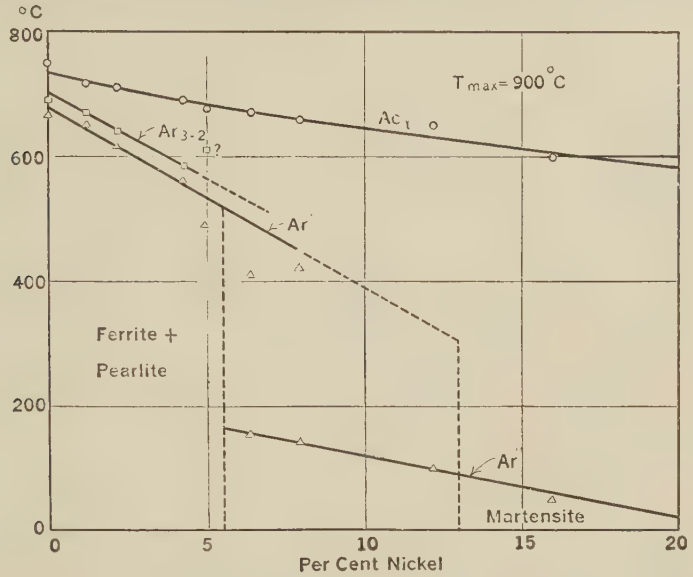


Fig. 286a. — Effect of nickel on the thermal critical ranges of 0.40 to 0.50 per cent carbon steels from data of Carpenter, Hadfield, and Longmuir. (Howard Scott.)

Fig. 287. — Nickel steel. Carbon about 0.30 per cent. Nickel about 3 per cent. Magnified 100 diameters. (G. A. Reinhardt, in the author's laboratory.)

the stability of cementite, causing it to graphitize more readily on annealing high carbon steel, possibly through the presence of some nickel in the carbide.

Treatment, Structure, and Properties. — The pearlitic nickel steels are those most widely used. In the majority of cases the nickel content does not exceed

3.50 per cent while the carbon content is seldom over 0.50 per cent. These steels compared with carbon steels of equal ductility have a considerably higher strength and especially higher elastic limit, while compared with carbon steels of like elastic limit they have much greater ductility. To explain this in another way, the introduction of some 3.50 per cent nickel in a 0.30 per cent carbon steel, for instance, raises its elastic limit very considerably while decreasing its ductility but slightly. Pearlitic nickel steels are also somewhat harder than carbon steels of like properties, hence better able to resist wear. When properly heat treated their ability to resist shocks is likewise greater. These valuable properties of nickel steel may be ascribed, in part at least, to the presence of stronger, harder, and tougher ferrite, and to finer grains. To obtain these results, however, the steel should be heat treated, that is, made finely sorbitic.

The structure of pearlitic nickel steel is shown in Figure 287. When examined under high magnification the nickel pearlite is seldom found as distinctly laminated as ordinary pearlite.

The hardening and annealing of nickel steels should be conducted at lower temperatures than the hardening and annealing of ordinary steels of similar carbon content since their critical points occur at lower temperatures. From the evidences at hand it would seem as if between 0 and 5 per cent nickel, and in the case of low carbon steels, each 1 per cent of nickel lowered the Ar_1 point some 20 deg. C. and the Ac_1 point some 10 degrees. In the nickel pearlitic steels of commerce, therefore, the points Ar_1 and Ac_1 should occur at or near the temperatures indicated in the following table according to their percentage of nickel.

% Ni	Ac_1	Ar_1
0	750	700
0.50	745	690
1.00	740	680
1.50	735	670
2.00	730	660
2.50	725	650
3.00	720	640
3.50	715	630
4.00	710	620
4.50	705	610
5.00	700	600

While nickel retards the carburization of iron by case hardening, the cores of nickel steel articles are not coarsened by the high temperature of the carburizing operation to the same extent as carbon steel cores, so that one treatment is often sufficient, namely, reheating to and quenching from a temperature slightly superior to the critical range of the case, that is, to some 700 to 750 deg. in the presence of some 3 or 3.5 per cent nickel. Higher nickel contents call for lower quenching temperatures.

The case hardening of nickel steels offers the possibility already alluded to of producing a martensitic case without quenching. Nickel steel, for instance, containing not over 0.25 per cent carbon and some 3.50 or more per cent nickel can readily be made martensitic near the outside by case hardening followed by air cooling, as

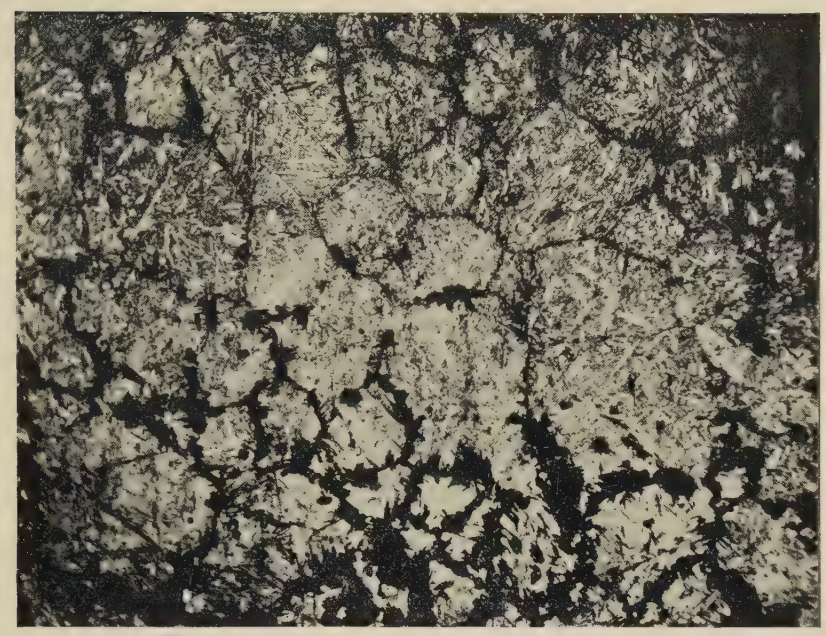


Fig. 288. — Nickel steel. Nickel 3.44 per cent. Carbon 0.176 per cent. Case hardened and air cooled. Magnified 100 diameters. (G. A. Reinhardt, in the author's laboratory.)

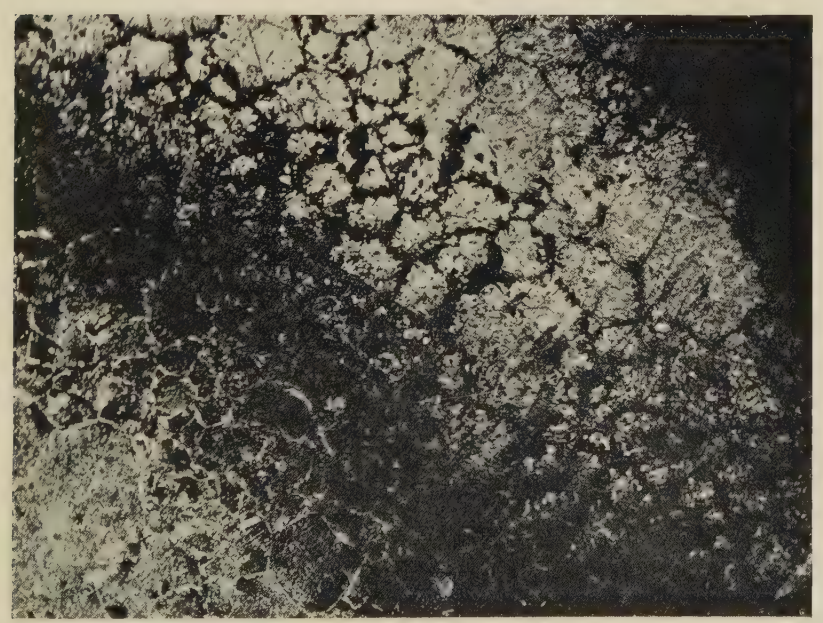


Fig. 289. — Same steel as in Figure 288. Same treatment. Magnified 50 diameters. (G. A. Reinhardt, in the author's laboratory.)

Fig. 290. — Nickel steel. Nickel 4.86 per cent. Carbon 0.115 per cent. Case hardened and air cooled. Magnified 100 diameters. (G. A. Reinhardt, in the author's laboratory.)

Fig. 291. — Same steel as in Figure 290. Same treatment. Magnified 300 diameters. (G. A. Reinhardt, in the author's laboratory.

shown in Figures 288 and 291. The martensitic grains owe their polyhedral form to the original austenitic grains from which they are derived. The thickness of the martensitic case is about 0.5 mm. The occurrence of troostite should be noted. Under lower magnification (Fig. 289) a solid troostite band is seen to separate the martensitic and the sorbito-pearlitic portions. With a little more carbon and nickel, martensito-austenitic cases may be produced, as shown in Figures 290 and 291.

Nickel steels that are martensitic as cast are not utilized because like all martensitic steels they are hard, brittle, and cannot be machined. Their case hardening should result in the formation of ductile, austenitic cases. Nickel steels which are

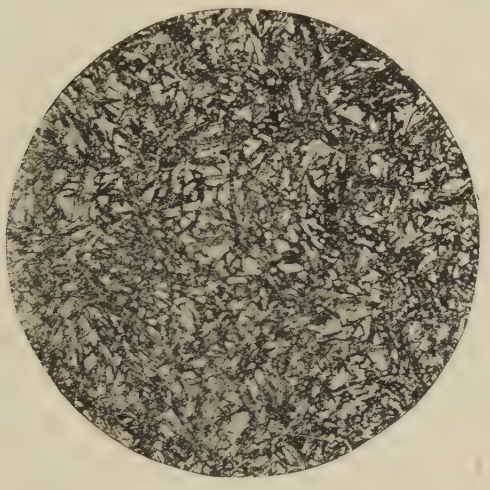


Fig. 292. — Nickel steel. Cast. Nickel 10 per cent. Carbon 0.80 per cent. Magnified 300 diameters. (Guillet.)

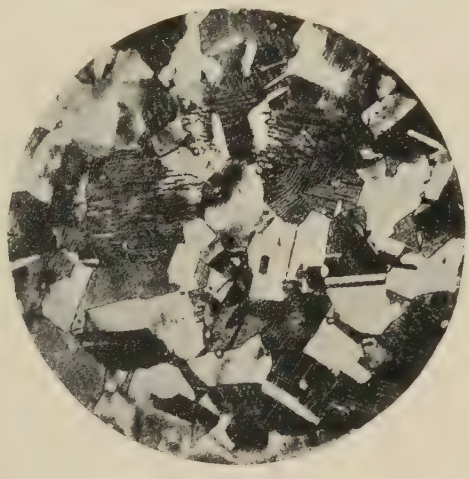


Fig. 293. — Nickel steel. Nickel 25 per cent. Carbon 0.80 per cent. Magnified 300 diameters. (Osmond.)

martensitic after air cooling may be troostitic, sorbitic, or even pearlitic after very slow cooling in the furnace, while they may become austenitic on water quenching. The structure of martensitic nickel steel is shown in Figure 292.

Austenitic nickel steels are not widely used, the high carbon, high manganese steels being preferred when an austenitic steel is desired, in part at least because of their lower cost. Like all austenitic steels they are non-magnetic, ductile, very difficult to machine, and have a low elastic limit. Their structure is polyhedral (see Fig. 293). The twinnings characteristic of gamma iron should be noted. Steels containing some 25 per cent nickel or more, however, hence austenitic, are used to make seamless tubes, and because of their resistance to corrosion, valve stems for internal combustion engines. Other types of austenitic nickel steels have found interesting applications based chiefly on the marked influence of nickel on the dilatation of the metal. With 36 per cent nickel, for instance, the dilatation is nealy nil and the resulting alloy, discovered by Guillaume, and called by him "invar," is used successfully for the construction of clocks and other instruments of precision. With some 46 per cent of nickel and 0.15 per cent carbon the coefficient of dilatation is nearly the same as that of glass, and alloys of that composition called "platinite" are used in place of platinum in the construction of incandescent electric lamps. Austenitic nickel steel may be made martensitic and thereby regain its magnetism

by immersion in liquid air. The increase of volume which accompanies this transformation produces a swelling of the polished surface which because of the resulting relief effect renders the structure of the metal apparent without etching, as shown in Figure 294.

Manganese Steel

Alloys of Iron, Carbon, and Maganese. — Manganese forms solid solutions both with gamma and alpha iron. In the presence of carbon, the carbide Mn_3C is formed, which practically contains the same percentage of carbon as Fe_3C, and probably

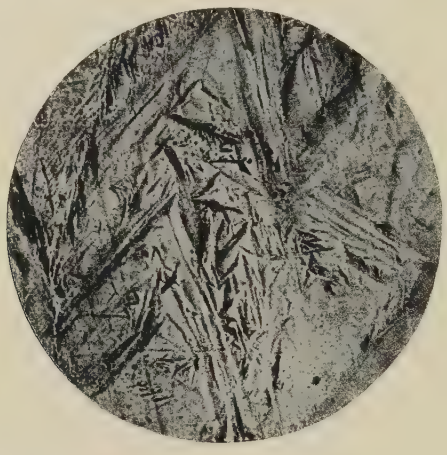


Fig. 294. — Nickel steel. Nickel 15 per cent. Carbon 0.80 per cent. Cooled in liquid air (−180 deg. C.). Not etched. Magnified 300 diameters. (Guillet.)

forms amorphous mixtures with the latter. At a high temperature these carbides are dissolved in gamma iron, and may be retained in solution by rapid cooling.

From this behavior of manganese the structural types formed by increasing both carbon and manganese may be anticipated. The steel should at first remain pearlitic and then become in succession martensitic and austenitic. With much manganese and carbon, however, separation of free carbides is to be expected. The constitutional diagram of manganese steels is shown in Figure 295 after Guillet, while a critical point structural diagram has been constructed tentatively in Figure 296. By comparing the constitutional diagram of manganese steel with that of nickel steel it will be noted that manganese is, roughly stated, twice as effective as nickel in producing a certain type of structure, as for instance in converting pearlitic into martensitic steel.

Influence of Manganese on the Critical Points. — The action of manganese on the critical points is shown in Figures 296a and 296b for steels containing respectively from 0.30 to 0.40 and from 0.7 to 1.00 per cent carbon, according to Dejean. Manganese decreases the percentage of carbon needed to produce eutectoid steel; with 2 per cent manganese, 0.75 per cent carbon suffices. Manganese also increases the hysteresis.

Treatments, Structure, and Properties. — Manganese is present in appreciable quantities in all ordinary carbon steels, but unless the latter contain considerably

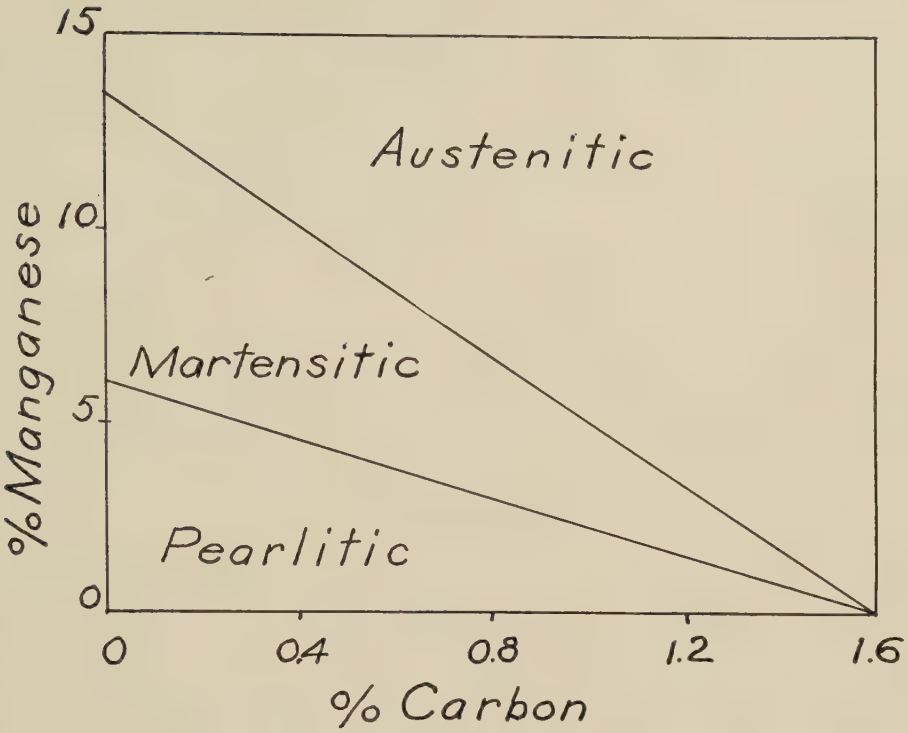


Fig. 295. — Manganese steel. Constitutional diagram. (Guillet.)

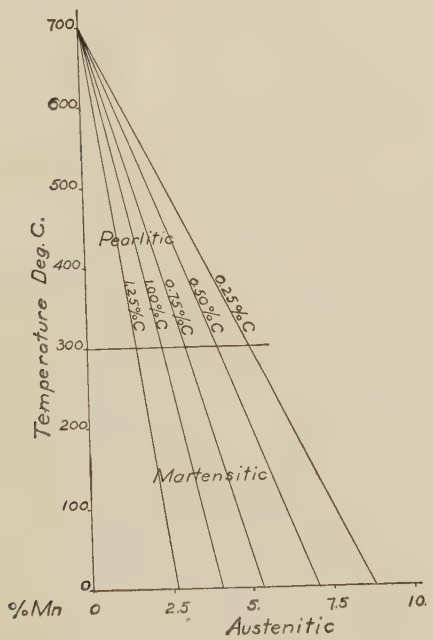


Fig. 296. — Influence of manganese and carbon on position of critical point Ar_1 and corresponding types of structure.

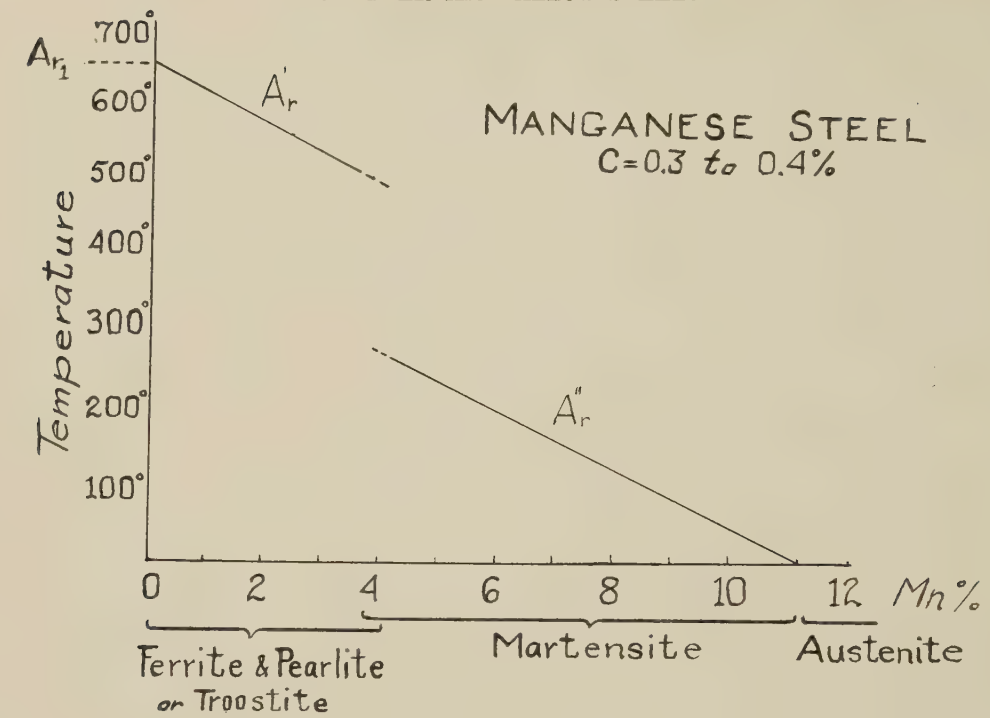


Fig. 296a — Influence of manganese on the Ar point. (Dejean.)

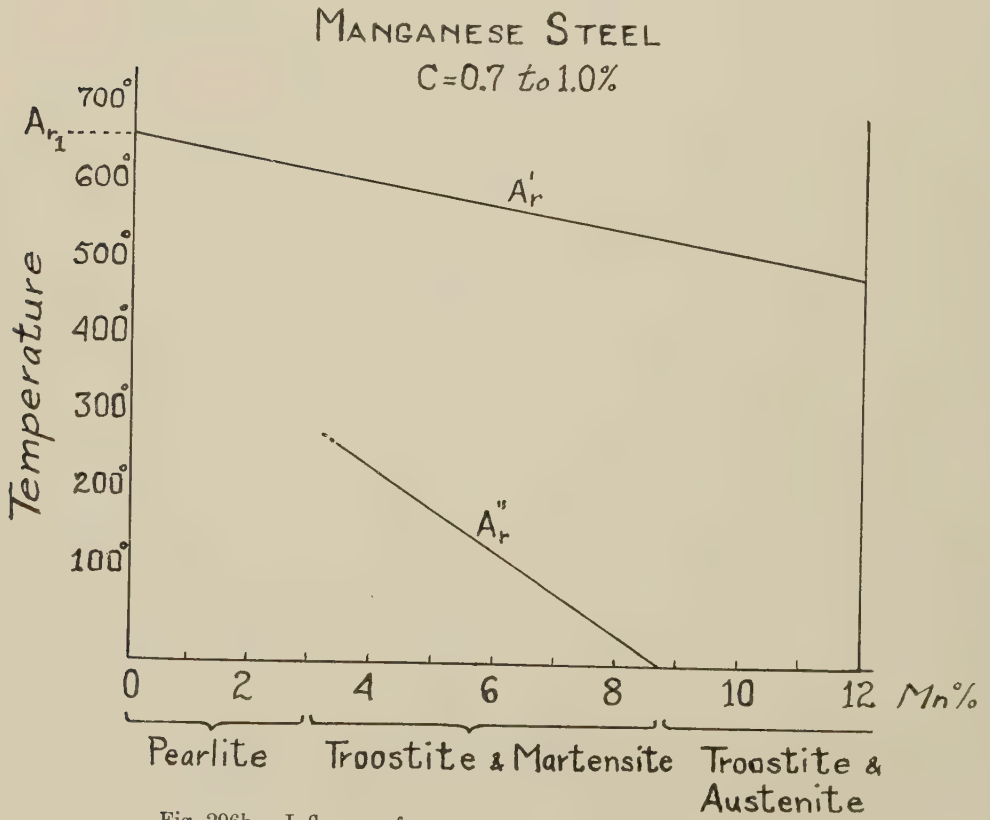


Fig. 296b — Influence of manganese on the Ar point. (Dejean.)

more than 1 per cent of that element they are not regarded as manganese steels. With carbon not exceeding 0.80 per cent and manganese not exceeding some 3 per cent the steels remain pearlitic and, therefore, not unlike the pearlitic nickel steels so widely used. Manganese pearlitic steels, however, have been practically ignored by steel manufacturers and users until quite recently, apparently (1) because of the widespread belief that such steels are brittle, and (2) because of the difficulty of manufacturing low carbon manganese steels. The belief in the brittleness of pearlitic manganese steels is founded on Hadfield's statement that between 2 and 6 per cent of manganese the steels are hopelessly brittle. On closer examination, however, it would seem as if this statement was true only in the case of rather high carbon steels cooled relatively quickly. Evidences have since been offered, notably by Guillet, showing that *low carbon* pearlitic manganese steel *slowly cooled* is not brittle.[1] These steels have been difficult to manufacture because of the necessity of using ferro-manganese from the blast furnace and therefore high in carbon, thereby introducing much carbon in the steel. At present, however, nearly carbonless ferro-manganese is produced in electric furnaces and also by the thermite process. It is also claimed that low carbon manganese steels can be successfully produced in the electric furnace under suitable oxidizing conditions and at high temperature, when carbon may be oxidized in preference to manganese. If the physical properties of low carbon pearlitic manganese steel are at all comparable to those of pearlitic nickel steel and if manganese steel can be manufactured more cheaply than nickel steel of like properties, the manufacture of low carbon manganese steel should receive more attention. Steel rails containing about 1.50 per cent manganese and 0.70 per cent carbon manufactured according to Hadfield's patent have given excellent results. Steel containing 1.50 per cent manganese and about 0.90 per cent carbon is claimed to deform less than steel containing smaller proportions of manganese. While manganese increases the strength and hardness of pearlitic steel and possibly its hardening power, it also increases the danger of cracks in the quenching bath. It increases the electrical resistance. The possibility of producing by case hardening articles having pearlitic cores and austenitic cases also deserves some consideration.

Martensitic manganese steels are not utilized because of the hardness and brittleness which they share with all martensitic steels. Those manganese steels whose composition is near the boundary line between the pearlitic and martensitic regions while martensitic after air cooling may be troostitic or even pearlitic after very slow cooling while they may become austenitic on quenching.

Austenitic manganese steel is of considerable industrial importance. It is often called from the name of its inventor "Hadfield" steel. It generally contains from 10 to 15 per cent manganese and from 1 to 1.5 per cent carbon. In its cast condition it is weak and has but little ductility, probably because of the presence of a considerable quantity of free carbide. On being heated to a high temperature (1000 deg. C. or more), however, and quenched in water or oil, its tenacity is greatly raised and it becomes very ductile; the treatment being often called on that account "water toughening." The marked change of properties resulting from it is probably due to the absorption of the carbide at a high temperature and its retention in solution by quick cooling. The structure of manganese steel both in its cast and in its water-quenched condition is shown in Figures 297 to 299. In the cast sample the carbide

[1] Arnold reports that steel containing less than 0.10 per cent carbon and 5.50 per cent manganese has a tensile strength of some 145,000 pounds per square inch and an elongation of 28.50 per cent.

is seen to occur as thick membranes surrounding the austenitic grains and here and there in chunks. The treated sample is nearly free from carbide and possesses the polyhedral structure characteristic of gamma iron and of austenite. According to

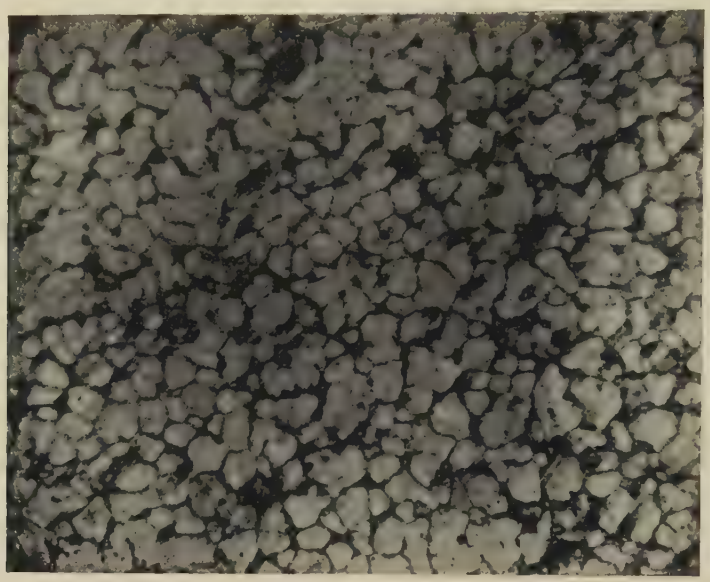


Fig. 297. — Manganese steel. Austenitic. Cast. Magnified 50 diameters.

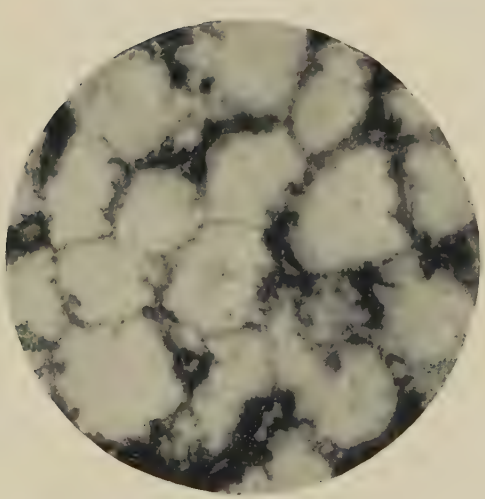


Fig. 298. — Same as in Figure 297. Magnified 300 diameters.

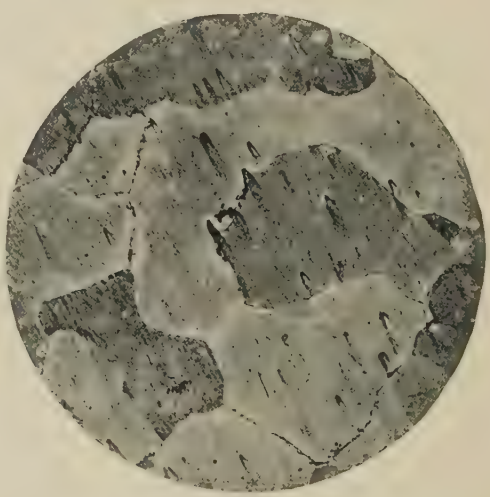


Fig. 299. — Manganese steel. Austenitic. Water quenched. Magnified 100 diameters.

Howe and Levy, the deformation lines so frequently observed in manganese steel after plastic deformation are slip bands (Fig. 200). The properties of austenitic manganese steel are those of austenite, namely, low elastic limit but great wearing power combined with much ductility.

The addition of some 0.6 to 2.50 per cent silicon to manganese steel of the usual Hadfield composition has been found by Sir Robert Hadfield to increase its toughness and resistance to perforation of thin sheets and to increase its fluidity and soundness. This improved manganese steel has been patented by the inventor.

In the water-quenched condition its tensile strength frequently exceeds 100,000 lbs. per sq. in., while the elastic limit varies generally between 50,000 and 55,000 lbs.

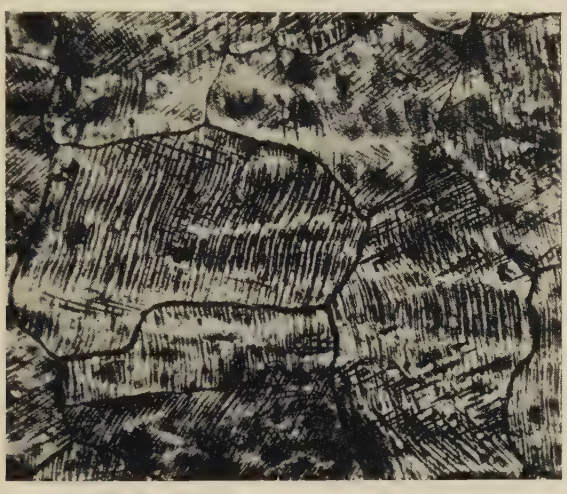


Fig. 300. — Deformation lines in manganese steel.

per sq. in. The elongation in 2 inches may exceed 30 per cent with a reduction of 35 to 40 per cent. The Brinell hardness is in the vicinity of 125. This hardness, however, increases greatly with deformation. In use, therefore, the surface becomes intensely hard, while it is backed by tough, ductile metal.

So-called silico-manganese steel containing 0.60 per cent to 0.70 per cent manganese, 1.50 to 2.0 per cent silicon, and about 0.50 carbon is used for springs and also for gears.

Chromium Steels

Alloys of Iron, Carbon, and Chromium. — Chromium dissolves in liquid iron and is retained in solid solution both in gamma and in alpha iron. In the presence of carbon it enters into chemical combination with that element to form according to different authorities: (1) independent carbides Cr_xC_y; (2) carbides forming isomorphous mixtures with iron carbides, Cr_xC_y, Fe_3C, or (3) double carbides $m\ Cr_xC_y \cdot n\ Fe_3C$.

Many forms of carbides have been reported as existing in chromium steel, to wit, by Arnold and Rhead: Cr_3C_2, Cr_4C, and the double carbide $2\ Fe_3C \cdot 3\ Cr_4C$; by Murakami $(Fe_3C)_{18}$, Cr_4C, $(Fe_3C)_9$, Cr_4C, and $Fe_3C \cdot Cr_4C$; by Carnot and Goutal, Fe_3C, $3\ CrC_2$, and $3\ Fe_3C \cdot Cr_3C$; by Williams, $3\ Fe_3C \cdot 2\ Cr_3C_2$, each writer having apparently demonstrated to his own satisfaction the accuracy of his deductions and the inaccuracy of others. Fortunately we need not take sides as it will suffice for our purpose to consider that these chromium carbides, whatever their exact formulæ, may dissolve in gamma iron at a high temperature and may be retained in solid solution at room temperature, partly at least, either in gamma iron when the steel remains austenitic, or in alpha iron when the steel becomes martensitic, in accordance with

the percentage of carbon and chromium present, the temperature from which the steel cools and the rate at which it cools. With a relatively small percentage of chromium, slow cooling may result in the rejection of the carbides and in the formation of a pearlitic or sorbitic matrix. All this is in agreement with the behavior of carbides outlined in the preceding chapter. The carbides of chromium may require for their diffusion prolonged heating at temperatures considerably in excess of the thermal critical range.

Influence of Chromium on the Critical Points. — According to Osmond and others, chromium raises Ar_1 and Ar_3 while having little influence on the position of

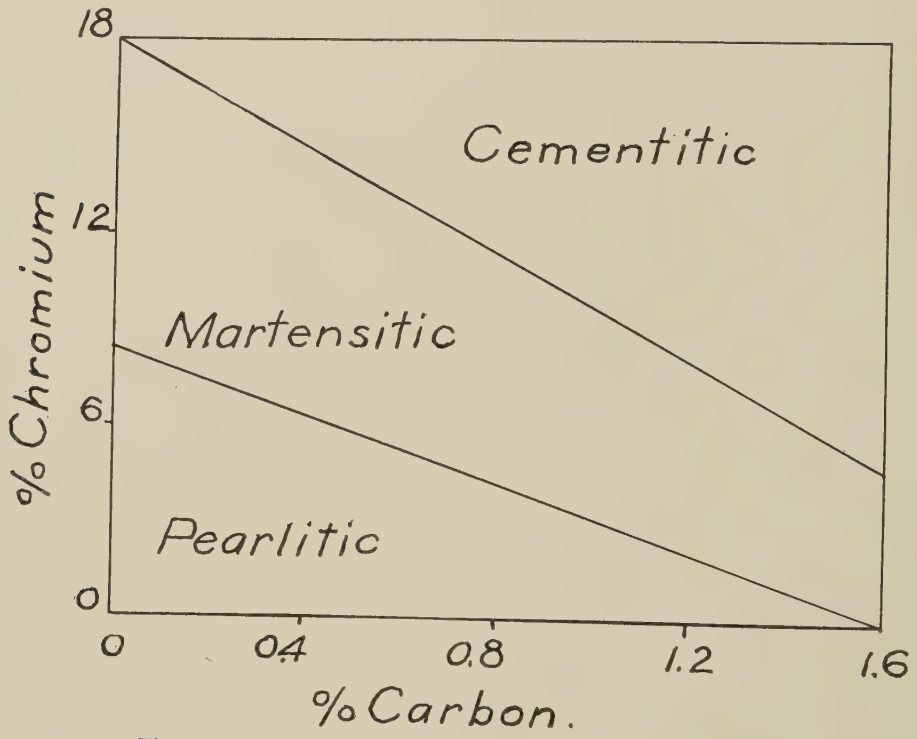


Fig. 301. — Chrome steel. Constitutional diagram. (Guillet.)

Ar_2, the Ar_1 point actually being lifted above the A_2 point. Experiments conducted at the Watertown Arsenal, Watertown, Mass., with steel containing 0.50 per cent carbon, also indicate that increasing the chromium content from 0 to 4.05 per cent raises the Ac_1 point from 743 to 791 deg. C. and the Ar_1 point from 671 to 748 deg. C. The action of T^{max} is greatly intensified, cooling from a high temperature resulting in hardening, probably by lowering the Ar_1 point to some 300 deg. C., the minimum critical quenching velocity, that is, the minimum speed of cooling required to produce hardening being the lower the higher the temperature from which cooling begins. Osmond, for instance, found the following relations between the maximum temperature and the position of the critical point on cooling:

Maximum Temperature	Critical Point on Cooling	Maximum Temperature	Critical Point on Cooling
835	713–716	1220	635–643
1030	682–692	1320	600–640

The constitutional diagram of chrome steels is shown in Figure 301 after Guillet.

Treatment, Structure, and Properties. — Chromium added to iron-carbon alloys increases the elastic limit, strength, and hardness, while it decreases ductility. It increases the hardening power and the depth of penetration. It promotes the stability of martensite, hence its value in cutting tools.

Chromium steels containing about 1 per cent carbon and 0.50 per cent chromium are used for chisels, files, drills, and saw blades, with 1.0 to 1.50 per cent chromium for ball bearings, and with some 15 per cent chromium for dies. Chromium steel is also used for armor-piercing projectiles.

The case hardening of chrome steels yields very hard cases. As the core coarsens, however, these steels should always receive the double treatment described in Chapter XVIII, that is, (1) reheating and quenching for refining the core, and (2) reheating and quenching for refining and hardening the case.

Becker writes that the hardness imparted by chromium is not accompanied by so much brittleness as that induced by carbon. The structure of pearlitic chromium steel resembles that of pearlitic carbon steel.

Chromium very greatly increases the resistance of iron-carbon alloys to atmospheric and water corrosion and to the action of food acids, and also to that of nitric acid.

It is upon this remarkable property of chromium that the manufacture of stainless steel is based. Stainless properties are imparted to iron-carbon alloys the more readily the less carbon they contain. For cutlery and like uses the steel generally contains about 0.30 per cent carbon and 12 per cent chromium. To secure stainlessness the steel should be quenched from a high temperature in order to cause the carbides to dissolve and to retain them in solution. So-called stainless iron is an iron-carbon alloy containing generally not over 0.10 per cent carbon and 10 to 15 per cent chromium. This metal does not need to be quenched from a high temperature in order to resist rusting, since it is practically free from carbides. With considerably higher percentages of chromium, even in the presence of much carbon, the alloys are stainless even after slow cooling. They cannot, then, however, be satisfactorily hardened by quenching since they remain austenitic, hence cannot be used for cutlery.

It will be mentioned elsewhere that large percentages of nickel, and at times some silicon, and indeed tungsten, manganese, and other elements, are added to these stainless irons and steels to increase their resistance to salt water, to hydrochloric, sulphuric, and other acids as well as to heat and to scaling.

Tungsten Steels

Alloys of Iron, Carbon, and Tungsten. — Tungsten dissolved in gamma iron at a high temperature remains dissolved in alpha iron at room temperature. When carbon is present it combines with that element. Some writers have reported with much positiveness the existence of various carbides and tungstides, such as $2\,Fe_3C \cdot 3\,WC$ (Williams), Fe_3C, WC, and Fe_3W (Carnot and Goutal), Fe_3C, WC, and Fe_2W (Arnold and Rhead), who claim also that double carbides are not formed, while Honda and Murakami state that they have "proved beyond doubt" the existence of a double carbide, $4\,Fe_3C \cdot WC$.

According to the percentage of carbon and of tungsten, the temperature from which cooling begins and the rate of cooling, (1) the carbides may be expelled from

solution and pearlite (or sorbite) formed, (2) the carbides may be retained in solution in alpha iron and martensite (plus troostite?) formed, or (3) the carbides may remain dissolved in gamma iron, the steel remaining untransformed, that is austenitic.

The constitutional diagram of tungsten steels is shown according to Guillet in Figure 302.

Influence of Tungsten on the Critical Points. — Osmond reports that in very low carbon steel at least, tungsten has little if any influence on the critical points.

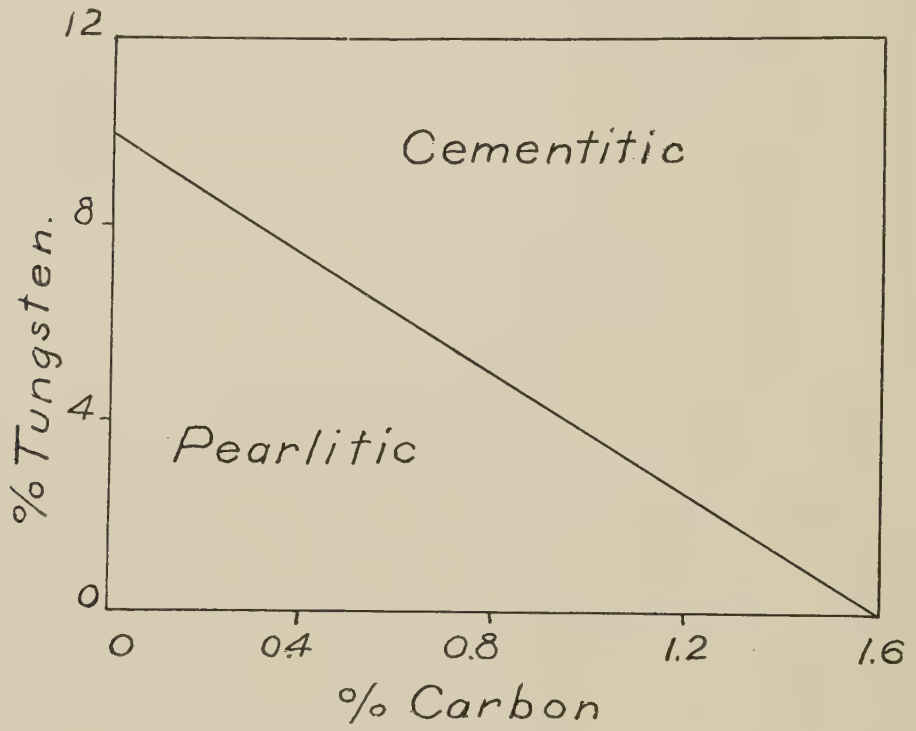


Fig. 302. — Tungsten steel. Constitutional diagram. (Guillet.)

It intensifies, however, the action of the temperature from which cooling begins (T^{max}). As this temperature increases, the Ar_1 point is progressively lowered, while the Ar_3 point disappears (Swinden). The position of the Ar_2 point remains unchanged or is slightly lifted. On heating, Ac_1 occurs at a higher temperature. Cooling a steel containing 0.42 per cent carbon and 6.25 per cent tungsten from 1015 deg., for instance, resulted in a faint critical point at 670 deg. while the lower point was depressed to 625 deg.; cooling from 1210 deg. caused the disappearance of the upper point while the lower remained very pronounced but now occurred at 500 degrees. Böhler, likewise experimenting with a steel containing 0.85 per cent carbon and 7.78 per cent tungsten, reports the existence of a point at 710 deg. and one at 550 deg., the upper one, however, occurring only when the metal has not been heated above 1100 deg. while the second is only to be detected when the temperature exceeds 1000 deg. In other words, on cooling from above 1100 deg. the lower point only occurs, on cooling from below 1000 deg. only the upper point is visible, while heating to and cooling from a temperature situated between 1000 and 1100 deg. causes the

appearance of both points. It will be shown soon that this indirect influence of tungsten upon the critical points suggests an explanation of the remarkable properties of self-hardening and high-speed steels which are chiefly tungsten steels.

Treatment, Structure, and Physical Properties. — When the carbides of tungsten are dissolved by heating to a sufficiently high temperature and retained in solution by a sufficiently rapid cooling, it is found that the grain has been refined and the cutting hardness increased, hence the value of tungsten steel for cutting purposes

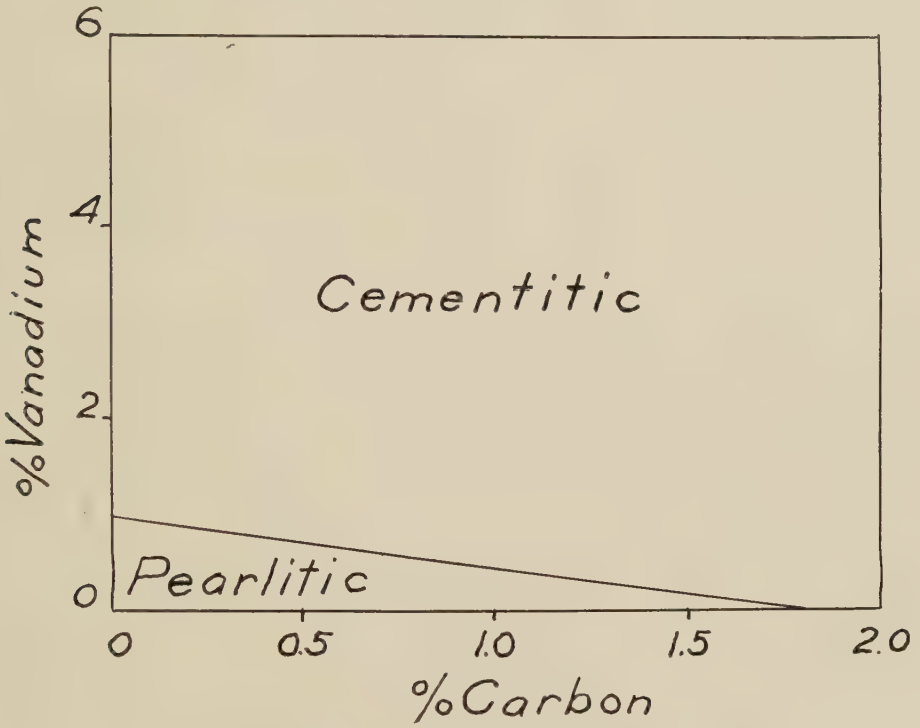


Fig. 303. — Vanadium steel. Constitutional diagram. (Guillet.)

as exemplified by Mushet steel, the precursor of modern high-speed steel. Air cooling is often sufficient to retain the carbides in solution while the metal becomes finely martensitic, i.e. tungsten steels are generally "self-hardening." Mushet steel contains about 1.50 per cent carbon, 7 to 8 per cent tungsten, and 1 to 2 per cent manganese. It is an air hardening steel and permits cutting at much greater speed than carbon steel tools. It is now known that if heated to a very high temperature its cutting properties are greatly improved, some of the characteristics of high-speed steel being acquired.

Some years later, the manganese present in Mushet steel was replaced by chromium at the Midvale Steel Company and elsewhere, and a better tool steel obtained, capable of still more rapid cutting. The discovery, announced in 1900 by Taylor and White, of the high heat treatment by which wonderful properties may be imparted to tungsten-chromium steels, followed by large increase in the contents of tungsten, decrease of carbon and of manganese, and, later, additions of vanadium, have given us the modern high-speed steel which has revolutionized the art of cutting metals.

Tungsten steel containing 1 to 2 per cent tungsten and 1 per cent carbon is used for chisels, with 3 to 6 per cent tungsten and 1.20 per cent carbon for finishing steel tools. With 1 to 3 per cent tungsten and 0.6 to 0.7 per cent carbon it is also used for liners of howitzers and other guns.

When introduced into a high carbon steel, tungsten imparts to the alloy high retentivity, coercive force, and hysteresis, hence its value for the manufacture of magnets, which generally contain 0.35 to 0.60 per cent carbon and 5 to 6 per cent tungsten.

Vanadium Steels

Alloys of Iron, Carbon, and Vanadium. — Vanadium forms solid solutions both with gamma and with alpha iron. In the presence of carbon, the vanadium carbide V_4C_3 is believed to form, and according to Arnold and Rhead, to displace Fe_3C in pearlite, until with 5 or 6 per cent vanadium, "vanadium pearlite" is formed, believed by them to be free from Fe_3C. Nicolardot mentions the formation of double carbides of Fe_3C and V_4C_3.

The constitutional diagram of vanadium steels is shown in Figure 303 after Guillet. Two types of structures are produced, pearlitic and cementitic. Guillet describes the appearance of the particles of free carbide as being triangular.

According to Guillet, heating cementitic vanadium steels to a high temperature fails to cause the absorption of the free carbide, vanadium steels differing in this respect from other steels in which double carbides are formed.

Action of Vanadium on the Critical Points. — The action of vanadium on the position of the critical points appears to be imperfectly known. There is little doubt, however, that when present in an amount not exceeding 0.2 per cent, both the Ar_1 and Ar_3 (or Ar_{32}) points are raised. It also increases hysteresis.

Treatment, Structure, and Properties. — Vanadium deoxidizes the molten steel, refines the grain, increases elastic limit, strength, hardness, and resistance to shock, to fatigue, and to wear. Added to chromium steel it enhances the valuable properties imparted to steel by chromium, hence the value of chrome-vanadium steel. It is quite possible that this beneficial effect of vanadium may be due, in part at least, to its powerful deoxidizing action.

Simple vanadium steels seldom contain more than 0.2 per cent vanadium,— they are not at present widely used, — the metal being added to other alloy steels and more specifically to chromium steel, to chrome-nickel steel, and to high-speed steel.

Silicon Steel

Alloys of Iron, Carbon, and Silicon. — Silicon combines with iron to form the compound FeSi, which in turn forms solid solutions both with gamma and with alpha iron.

The constitutional diagram of silicon steels is shown in Figure 304 according to Guillet. It will be seen that the structure is independent of the carbon content, being entirely regulated by the proportion of silicon. As long as the proportion of silicon does not exceed 5 per cent the steel is pearlitic and the whole of the carbon remains in the combined condition. Between 5 and 7 per cent of silicon some pearlite is still present, and hence some combined carbon, but graphitic carbon also occurs; between 7 and 20 per cent of silicon the whole of the carbon is in the graphitic condi-

tion, the balance of the steel consisting of a solid solution of the silicide FeSi in iron (silico-ferrite), and also, according to Guillet, of some Fe_2Si likewise dissolved in iron. With more than 20 per cent of silicon the steel is composed of graphite and of FeSi.

Influence of Silicon on the Critical Points. — Silicon raises both the A_3 and the A_1 points, the former disappearing according to Charpy and Cornu-Thénard for a

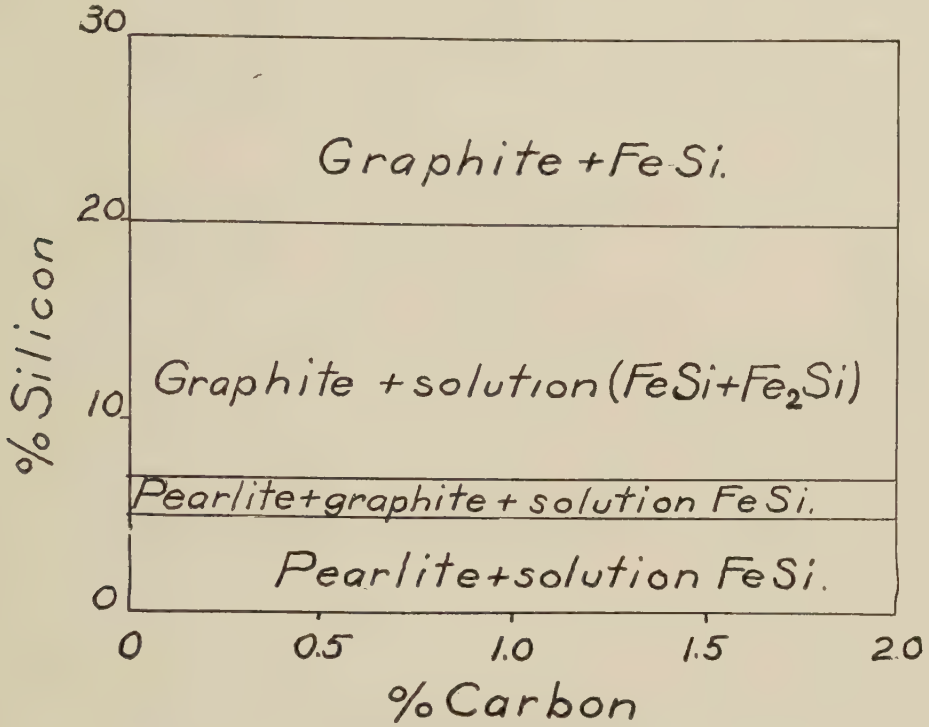


Fig. 304. — Silicon steel. Constitutional diagram. (Guillet.)

content of 1.50 per cent, the latter at about 5 per cent silicon. Osmond writes that the A_2 point is lowered, and this has been confirmed by Charpy and Cornu-Thénard.

Treatment, Structure, and Properties. — Silicon increases the elastic limit, decreases the ductility, and results in a coarse-grained structure. It decreases the solubility of carbon in iron and promotes the graphitizing of cementite. According to Charpy and Cornu-Thénard, iron containing 4 per cent silicon cannot absorb carbon below 900 deg. C. and with 7 per cent silicon it cannot absorb it below 1000 deg. C.

Silicon exerts notable influences on the electric and magnetic properties of iron. It increases the electrical resistance, reduces the coercive force and retentivity (hence the hysteresis). It increases permeability for magnetizing power below saturation and reduces core losses (hysteresis and eddy currents). It is why silicon steel containing about 4 per cent silicon is used so extensively for transformer sheets.

The presence of 4 per cent silicon practically eliminates the action of aging, that is the core loss does not increase after long service in transformers. It is claimed that by melting this silicon steel (or commercially pure iron) in vacuum so as to extract the dissolved gases the hysteresis loss is reduced to a quarter or less of the original value (C. H. Desch).

Silicon increases the resistance of iron to the action of acids, hence its use in some non-corroding steels and cast irons. As already mentioned, steels containing 1 to 2 per cent silicon, 0.60 per cent to 0.70 per cent manganese, and about 0.50 per cent carbon, known as silico-manganese steels, are used for springs and also for gears.

It should be noted that the only silicon steels utilized contain less than 5 per cent of silicon and are, therefore, pearlitic and free from graphitic carbon, unless indeed subjected to prolonged annealing or very slow cooling, when some graphitic carbon

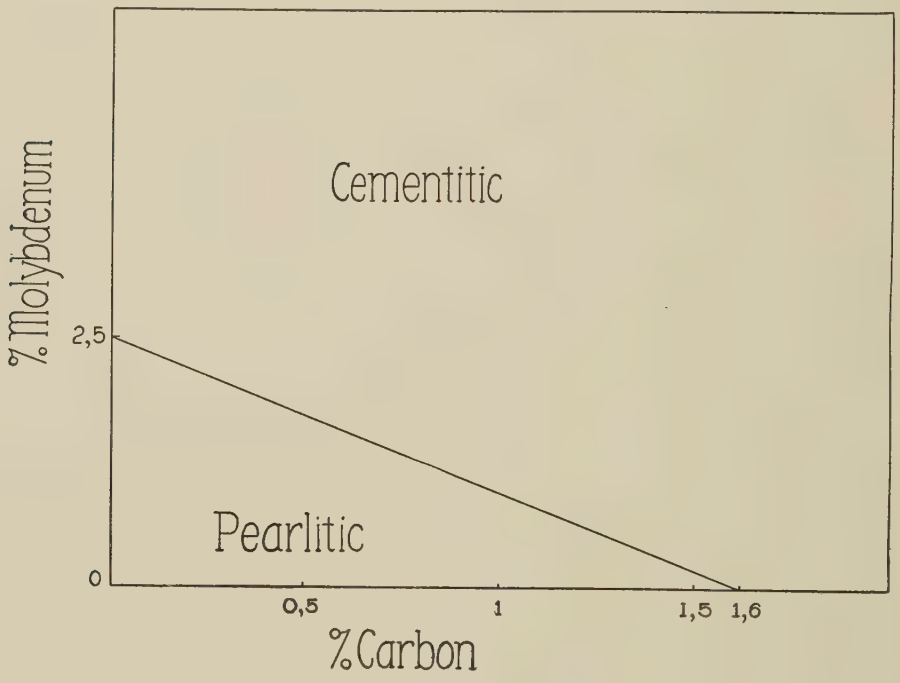


Fig. 305. — Molybdenum steel. Constitutional diagram. (Guillet.)

will form, especially in high carbon steels. This formation of graphitic carbon takes place the more readily the higher the temperature, the longer the time at a high temperature, the more silicon and the more carbon in the steel.

Molybdenum Steels

Alloys of Iron, Carbon, and Molybdenum. — Molybdenum dissolves both in gamma and in alpha iron. In the presence of carbon the existence of the double carbide $Fe_3C \cdot Mo_2C$ has been reported by Goutal, the carbide Mo_2C by Nicolardot, and the compound $Fe_3Mo_6C_2$ by Arnold and Rhead.

These carbides may be dissolved at a high temperature in gamma iron and retained in solution at room temperature either in gamma iron (austenitic steel) or in alpha iron (martensitic steel) according to the percentage of carbon and of molybdenum, the temperature from which cooling starts, and the rate of cooling. Slow cooling in the presence of a relatively small amount of molybdenum will of course result in the separation of the carbides and in the formation of a pearlitic or sorbitic

matrix. The constitutional diagram of molybdenum steels is shown after Guillet in Figure 305. With increasing carbon and molybdenum, the steels which were at first pearlitic on slow cooling become cementitic.

Influence of Molybdenum on the Critical Points. — Molybdenum seems to affect the positions of the critical points very much as tungsten does. According to Thomas Swinden, the Ar_1 point is steadily lowered as the temperature from which cooling starts increases, that lowering being the more marked the larger the percentages of molybdenum and carbon.

Treatment, Structure, and Physical Properties. — Molybdenum appears to influence the properties of iron-carbon alloys in a way similar to that of tungsten, its action, however, being more drastic. It is stated that one part of molybdenum will have the same effect as two or three parts of tungsten. The high price of molybdenum is probably responsible, in part, for its not being used more extensively in the manufacture of alloy steels, although the trouble encountered with seaminess may also be responsible.

It decreases the percentage of carbon needed to produce eutectoid steel. According to Guillet, with 8 per cent molybdenum, 0.40 per cent carbon suffices. To quote Hoyt: "At the present writing (1921) the future of molybdenum in steel metallurgy seems to be in its use in chrome-molybdenum or chrome-nickel-molybdenum steels for automobile or airplane service where particularly high-grade steels are required, and possibly in its use in high-speed steel." Molybdenum steel is also used for magnets.

Copper Steels

Alloys of Iron, Carbon, and Copper. — Copper forms solid solutions with gamma iron above the critical range, and with alpha iron below that range. In the presence of carbon, copper remains in solution.

Although at one time copper was invariably held to cause red-shortness, it is now admitted that as much as 0.5 per cent of copper may be present in steel without detriment and some place the upper limit much higher.

Seeing that copper behaves like nickel in forming a solid solution with ferrite and in its action on the position of the critical points which it tends to lower, it might be expected that copper steels should have properties somewhat comparable to those of nickel steels. Indeed, it is claimed by some that that expectation is fulfilled, up to 3 per cent copper; with a larger percentage of copper, the steel is undoubtedly red-short.

The addition of some 0.15 to 0.30 per cent copper to mild steel increases its resistance to corrosion under *certain* atmospheric conditions. The claims that they are more resistant under all atmospheric conditions is not warranted. Those steels are known as copper-bearing steels.

Hoyt suggests the addition of Monel metal (one part copper plus two and one-half to three parts of nickel) to steel to produce cupro-nickel steels, resembling in their properties higher nickel, hence more expensive steels.

Chrome-Nickel Steels

Alloys of Iron, Carbon, Nickel, and Chromium. — In the alloys of iron, carbon, nickel, and chromium, known as "chrome-nickel steels," the nickel is dissolved in

the iron (gamma or alpha) while the chromium is combined with the carbon. These carbides of chromium may be dissolved in the gamma iron already holding nickel in solution and may be retained in solution at room temperature in gamma iron (austenitic steel) as in alpha iron (martensitic steel), or they may be rejected from solution with the formation of pearlite or of sorbite.

It is natural to expect that the properties of chrome nickel steels will partake of the properties of both nickel steels and chromium steels already outlined.

From our knowledge of the constitution of nickel steels and of chromium steels it is possible to foretell the constitution of the quaternary chrome-nickel steels. Nickel steels being pearlito-martensito-austenitic and chrome steels being chiefly pearlito-cementitic, we may expect that in chrome-nickel steels, as the proportions of carbon, nickel, and chromium increase, the steels, at first pearlitic, will become in turn martensitic, austenitic, and cementitic. In the case of cementitic steels the free carbides will be embedded in a martensitic or austentitic matrix according to their composition. It should also be expected that increasing the proportion of nickel (and carbon) will cause the steel to pass from the pearlitic to the martensitic condition, etc., while increasing the chromium (and carbon) will make it cementitic. The presence of both nickel and chromium in the same steel produces a metal possessing the valuable qualities of both nickel and chromium steels, namely, high elastic limit combined with high ductility, greater hardness, hardening power, resilience, and better wearing qualities than carbon steels. Chrome-nickel steels are especially valuable in the construction of parts to be hardened and tempered when they yield a finely martensitic structure having greater shock-resisting power than the martensite of carbon steels. Practically the only chrome-nickel steels utilized are the pearlitic ones containing therefore moderate amounts of carbon, nickel, and chromium. They are used extensively in automobile construction and for the manufacture of armor plates. In the latter case, of course, one face of the plates is subjected to the case-hardening treatment. The case hardening of nickel-chromium steel resembles that of nickel steel. The metal should be reheated, after the case-hardening operation, slightly above the critical range of the case and quenched. Because of the presence of nickel it is not so imperative to heat to and quench from a temperature superior to the critical range of the core before hardening the case, although such procedure would probably yield a tougher core.

By adding chromium to nickel steel the hardness is increased as well as the hardening power and depth of the hardened layer after quenching. Resistance to wear is likewise increased and the grain is finer. Nickel-chromium steels are more sensitive to heat treatment than plain nickel steel and more resistant to shocks and to fatigue. The steels mostly used contain generally from 1 to 3.5 per cent nickel, from 0.5 to 1.5 per cent chromium, and 0.30 to 0.50 per cent carbon. Air-hardening chrome-nickel steels are also used. Steels belonging to this class generally contain more than 5 per cent carbon, nickel, and chromium, taken in the aggregate, and not less than 0.30 per cent carbon. Finally, steels containing very high proportions of nickel and chromium are employed because of their resistance to corrosion, to scaling, and to high temperatures. They may contain as much as 40 per cent nickel and 5 to 20 per cent chromium. Some of these may also contain a considerable amount of manganese, or of silicon, or of both.

Armor plates and armor-piercing projectiles frequently contain in the vicinity of 0.35 per cent carbon, 4 per cent nickel, and 2 per cent chromium.

For case-hardening purposes, nickel-chromium steels should not contain much more than 0.20 per cent carbon.

The nickel-chromium steel known as Mayari steel is obtained from the refining of Mayari pig iron, itself resulting from the smelting of iron ore from the Mayari mine in Cuba. The pig iron contains 1.3 to 1.50 per cent nickel and 2.50 to 3 per cent chromium, and the steel 1 to 1.50 per cent nickel and 0.20 to 0.70 per cent chromium, a large loss of chromium through oxidation necessarily occurring in the treatment of the pig iron.

It has been reported by several investigators that some chrome-nickel steels after being hardened and drawn between 450 and 700 deg. C. followed by *slow cooling* from the drawing temperature become brittle, whereas if *quenched* from the drawing temperature they acquire a normal toughness. It has been further observed that of two steels of practically the same chemical composition, one may suffer from this brittleness, while the other may be free from it. To the present time, no relation has been discovered between this phenomenon and the chemical composition of the steel. It is called by some, improperly it would seem, "blue brittleness."

Ternary and Quaternary Vanadium Steels. — The introduction of a small amount of vanadium into various special steels has been strongly urged and nickel-vanadium, chrome-vanadium, molybdenum-vanadium, chrome-nickel-vanadium, and chrome-tungsten-vanadium steels have been used. It is claimed that the presence of a small proportion of vanadium (less than 0.50 per cent) increases the soundness of castings and their freedom from occluded gases and that it adds to the desirable physical qualities of forgings such as strength, resilience, ductility, etc. Guillet writes that nickel-vanadium steel properly hardened by quenching is relatively so tough that unlike other hardened steels it does not require tempering. These steels will be pearlitic, martensitic, or austenitic according to their composition and the treatment they receive. The chrome-vanadium steel is probably the most widely used of the vanadium steels.

In chrome-vanadium steels the percentage of vanadium generally varies from 0.15 to 1 per cent. If the steel is to be case hardened, it should not contain much over 0.20 per cent carbon. For parts to be heat treated, the carbon varies generally between 0.25 and 0.40 per cent.

Chrome-vanadium steel is used for driving axles and other forgings for locomotives, and for automobile springs and axles which are called to withstand repeated alterations of stress in the neighborhood of the elastic limit without taking a permanent set. The steel has also been applied to the maunfacture of torpedo tubes, compressed air flasks, gun forgings, and the like (Hadfield).

Some 0.20 per cent vanadium is sometimes added to nickel-chromium steel. It is believed to refine the grains and to accentuate the valuable properties of nickel-chromium steel.

Chrome-molybdenum and chrome-nickel-molybdenum steels, both with and without addition of vanadium, have been used especially for automobile construction.

High-Speed Steels

Alloys of Iron, Carbon, Tungsten, and Chromium. — High-speed steels are essentially alloys of iron, carbon, tungsten, and chromium. It has been seen that both tungsten and chromium combine with carbon and that the resulting carbides dissolve

in gamma iron at a high temperature. The solid solution may be retained untransformed at room temperature (austenite) or it may be converted through partial transformation into a solid solution of the carbides in alpha iron (martensite). On slow cooling the carbides crystallize out of solution.

According to Arnold and Rhead, the following compounds may exist in high-speed steels: Fe_3C; CrC, WC, Fe_3W, and V_4C_3.

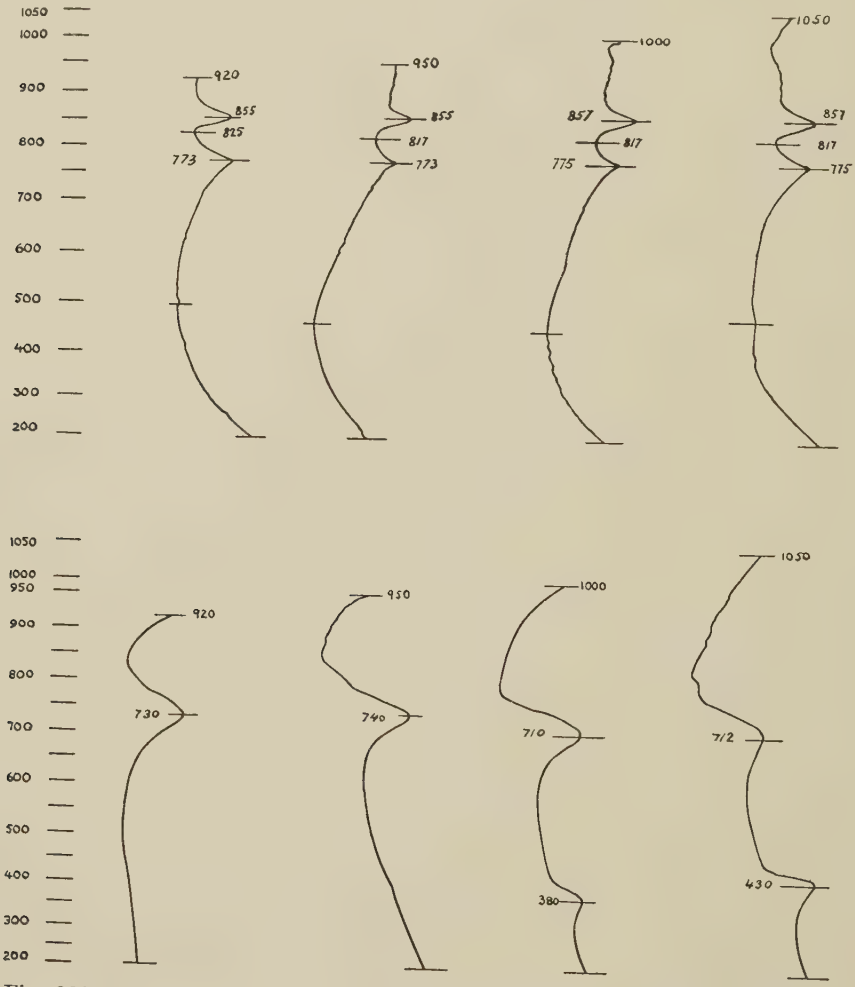


Fig. 306. — Heating and cooling curves of high-speed steel. Slowly cooled in furnace. Time of cooling from 1000 to 200 deg. C., 132 minutes. (M. Yatsevitch, in the author's laboratory.)

Critical Points of High-Speed Steel. — Yatsevitch has conducted in the author's laboratory an extensive investigation of the influence of heat treatment upon the position of the critical points of high-speed steel. Over 100 heating and cooling curves were taken with a Saladin-Le Chatelier recording thermo-electric pyrometer. The most significant results are here briefly outlined. The steel used, kindly supplied by Dr. J. A. Mathews, had the following compositions: tungsten 18.20 per cent, chromium 3.00 per cent, vanadium 0.95 per cent, silicon 0.27 per cent, carbon 0.62

per cent, manganese 0.38 per cent, sulphur less than 0.025 per cent, and phosphorus less than 0.025 per cent. Heating curves obtained on heating this steel respectively to 920, 950, 1000, and 1050 deg. C. are shown in Figure 306, as well as the cooling curves resulting from slow furnace cooling from these temperatures.

The heating curves exhibit two critical points respectively at about 775 and 855 deg. C. These points were found to be remarkably constant. Occurring as they do within such narrow range of temperature (some 80 deg. C.) it might be asked if instead of indicating two distinct transformations they do not correspond to two phases or stages of the same transformation.

The curves obtained on cooling slowly from 920 and 950 deg. C. respectively indicate a sharp evolution of heat occurring at 730 to 740 deg. C. which we naturally infer to correspond to the opposite phase of the transformation or transformations occurring on heating as indicated by the heating curves. So long as the temperature reached on heating does not exceed 950 deg. C. the curves obtained on slow cooling are of the same type, i.e. they exhibit but one well-marked critical point at 730 to 740 deg. C. When, however, the maximum temperature on heating, which for brevity and following Howe may be called T^{max}, reaches 1000 deg. C., this thermal point is slightly *lowered*, while a second point occurs whose position although shifting somewhat, remains in the vicinity of 400 deg. C. (Fig. 306). As T^{max} increases, the upper point of the curve obtained on *slow* cooling decreases in intensity, while the intensity of the lower point increases. Bearing in mind that as T^{max} increases we are approaching the treatment needed to confer high-speed hardness, we are justified in inferring that the transformations indicated by the upper point on cooling must be thoroughly suppressed in order to obtain the desired results and that this suppression is to be brought about (1) by high heating and, as will be shown presently, (2) by rapid cooling.

The influence on the cooling curves of rapid cooling from increasingly high temperatures is clearly written in the curves shown in Figures 307 and 308. The curves of Figure 307 were obtained by cooling freely in air the specimens and the tubes in which they were heated; those of Figure 308 by cooling in the same manner but more rapidly by means of a fan.

With the first rate of cooling (Fig. 307) it will be noted that (1) on cooling from 800 deg. C. but one sharply marked evolution of heat occurs on cooling at 665 deg. C., (2) on cooling from 850, a critical point occurs in the curve at 245 deg. C., and (3) on increasing T^{max} up to 1000 deg. C. the upper point on cooling is somewhat lifted but greatly decreases in intensity and shows signs of being finally eliminated, while the lower point is gradually raised to 370 deg. C. and becomes very intense. On cooling from 900 deg. C. the two points appear to have nearly the same intensity.

When cooling at the more rapid rate indicated by the curves of Figure 308 the same occurrences are observed but still more intensified. Cooling from 1000 deg. C., for instance, shows an intense point at 395 deg. C. while the upper transformation if it still takes place is much more feeble besides being gradual and covering a wide range of temperature (730 to 460 deg. C.).

Summing up, it seems evident that with increasing T^{max} and rate of cooling the upper critical point of the cooling curves is nearly, if not entirely, suppressed while the lower point grows enormously in intensity. The inference appears warranted that the treatment imparting high-speed hardness suppresses, at least for the major part, a certain transformation occurring normally on slow cooling from moderately

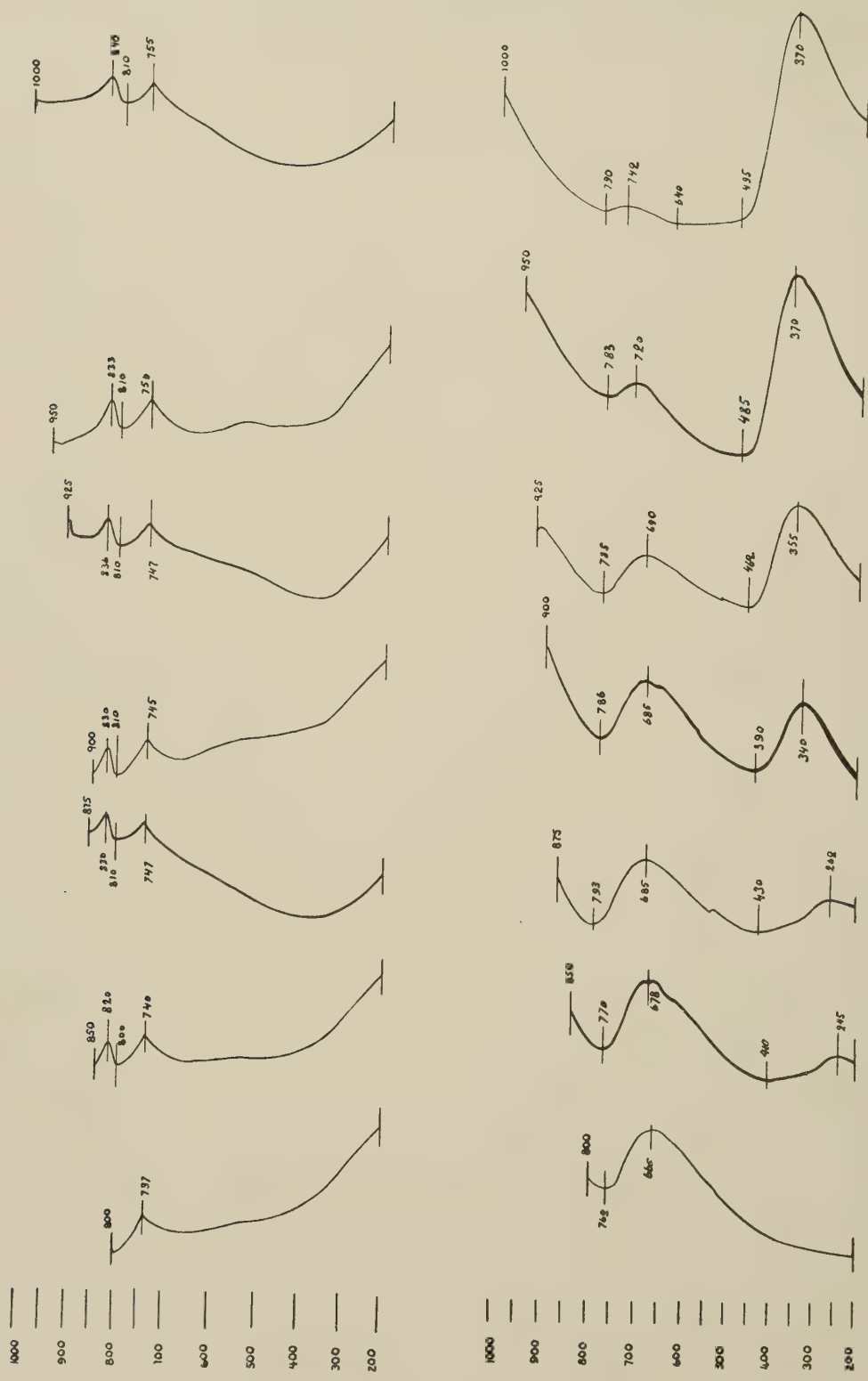


Fig. 307. — Heating and cooling curves of high-speed steel. Samples cooled freely in air in the tubes holding them. Time of cooling from 1000 to 200 deg. C., 13½ minutes. (M. Yatsevitch, in the author's laboratory.)

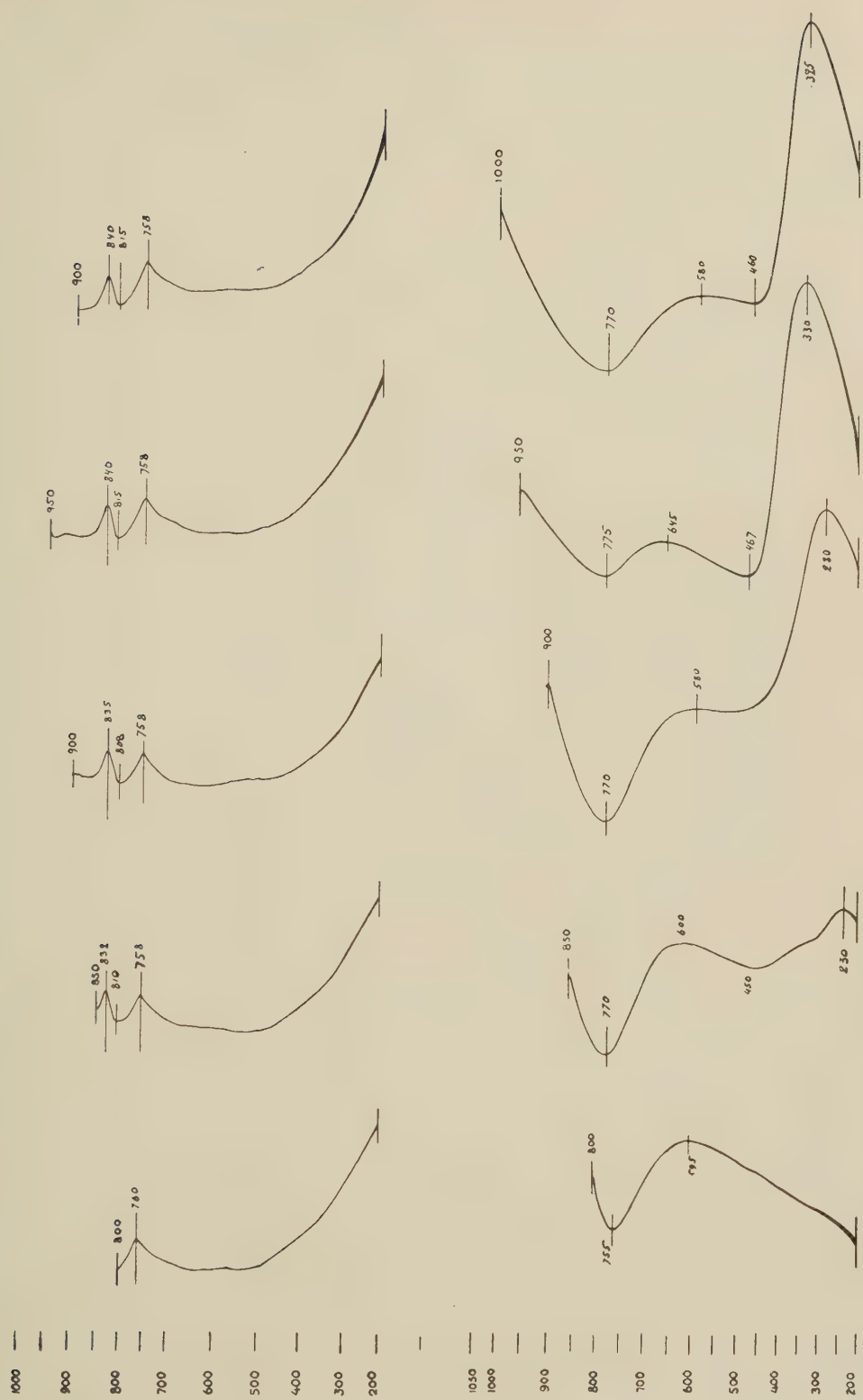


Fig. 308. — Heating and cooling curves of high-speed steel. Samples cooled in air in the tubes holding them. Cooling hastened by fanning. Time of cooling from 1000 to 200 deg. C., 6½ minutes. (M. Yatsevitch, in the author's laboratory.)

high temperatures at about 730 deg. C., while inducing with increasing magnitude a new transformation generally between 350 and 400 deg. C. We naturally associate the upper point with the allotropic transformation of iron accompanied by the separation of the carbides, and the lower one with the allotropic transformation only, the carbides being retained in solution. If this view is correct, high-speed steel should then be martensitic.

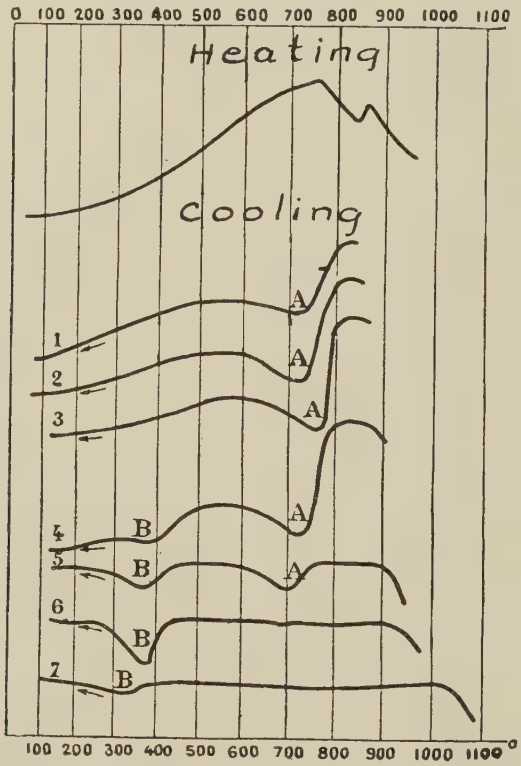


Fig. 309. — Critical points of high-speed steel. (Dejean.)

Cooling curves resembling those of Yatsevitch have been obtained by P. Dejean [1] (Fig. 309). They result from cooling a high-speed steel containing 18 per cent tungsten and 4 per cent chromium at the same rate but from progressively higher temperatures. So long as the temperature remains inferior to 900 deg. C. the curves exhibit but one critical point, termed *A* by the author, between 700 and 800 deg. C. Increasing the temperature causes the appearance of a second point, *B*, between 300 and 400 deg. C., and finally the complete disappearance of the point *A*. The authors conclude that when the cooling curves exhibit only the point *A*, the steel is troostitic or pearlitic. When both *A* and *B* occur, the steel contains both troostite and martensite, while when the point *B* only is present, the metal is wholly martensitic. This phenomenon recalls the gradual elimination of the point A′r and the sudden occurrence of the point A″r, when quenching carbon steel as described in Chapter XIV, the point A′r corresponding to the formation of troostite, and A″r to that of martensite. A similar phenomenon is observed in the cooling of any self-hardening steel.

[1] Comptes Rendus, July, 1917.

Treatment, Structure, and Properties. — Slowly cooled chrome-tungsten steels are cementitic with a pearlitic, sorbitic, or even troostitic matrix. Upon being heated to a high temperature the carbide particles are dissolved, at least for the most part, and if the cooling that follows be sufficiently rapid they are retained in solution, the metal acquiring a finely austenitic, martensitic, or austenito-martensitic structure. To cause a complete absorption of the free carbide, however, a very high temperature is often required, in some cases approaching the melting point

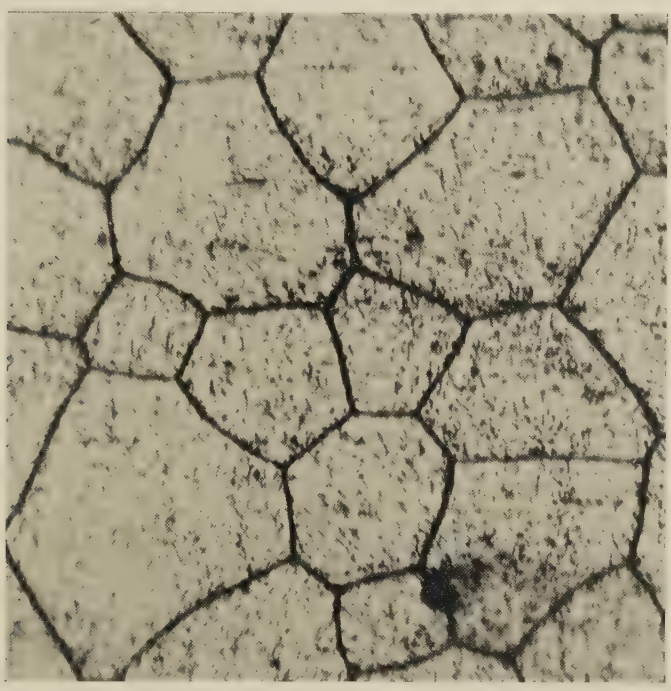


Fig. 310. — High-speed steel. Quenched in air blast at 1160 deg. C. Magnified 500 diameters. Tungsten about 13 per cent. Chromium about 4 per cent. Carbon 0.46 per cent. (H. B. Pulsifer.)

of the steel, while air cooling is frequently sufficiently rapid to prevent the carbide from again forming. After such treatment these steels although fully hardened are in a condition relatively so stable that they may be heated to a visibly red heat, i.e. to some 600 deg. C., before undergoing any marked softening. This invaluable property makes it possible, with tools made of such steels suitably treated, to cut steel and other hard metals at such speed that the cutting edge of the tool becomes visibly red-hot before breaking down. These steels are known in consequence as high-speed steels. Their discovery by Taylor and White, at the time in the employ of the Bethlehem Steel Company, marks one of the most distinct and revolutionary advances ever made in the metallurgy of iron and steel. Suitably treated high-speed steel often exhibits a polyhedral (austenitic?) structure (Fig. 310) quite free from carbide particles. In the presence of large amounts of tungsten and chromium, however, some carbide remains undissolved even after rapid cooling from a temperature close to the melting point of the metal (Fig. 311). The presence of a moderate amount

of free carbide after the high-heat treatment is not considered detrimental; on the contrary it appears to increase the cutting properties of the metal.

In the annealed condition the steel contains carbide particles which are probably the more numerous the larger the percentage of tungsten and chromium present (Figs. 312 and 313).

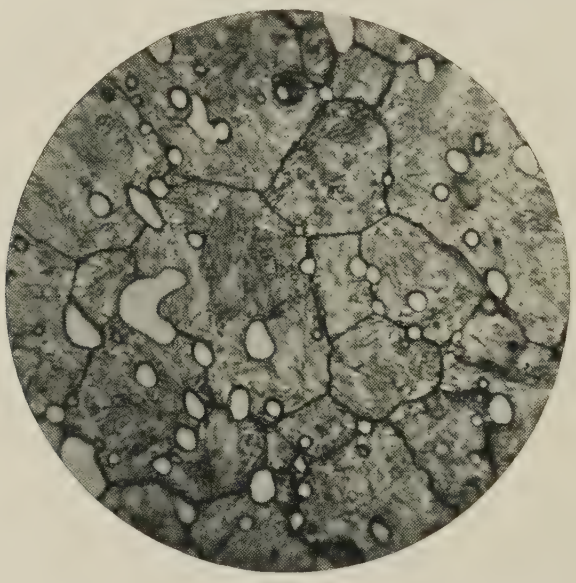


Fig. 311. — High-speed steel. Quenched at 1280 deg. C. Magnified 1500 diameters. Tungsten 17.87 per cent. Chromium 3.46 per cent. Vanadium 0.81 per cent. Carbon 0.65 per cent. (J. V. Emmons.)

Modern high-speed steels generally contain 0.30 to 0.75 per cent carbon, 12 to 20 per cent tungsten, 4 to 7 per cent chromium, about 1 per cent of vanadium, and not over 0.40 per cent manganese.

With one or more per cent of vanadium it is possible to decrease materially the percentage of tungsten without impairing the cutting hardness. With more than 2 per cent vanadium the steel becomes brittle.

Molybdenum has been added, with at times very good results, while at other times the steel was not satisfactory. The use of that element in high-speed steel has not yet fully emerged from the experimental stage. Cobalt, also, and uranium have been tried and superior results claimed, but more experimental data will have to be accumulated to justify their use.

It should be borne in mind that high-speed steel even if it contains but 0.30 per cent carbon is decidedly hyper-eutectoid, hence the abundance of carbides when slowly cooled.

The discoverers of high-speed steels recommended the following treatments as yielding the best results: (1) heating the tool slowly to about 815 deg. C., then quickly until its extreme edge showed indications of melting, (2) cooling the tool quickly to below 860 deg. and then quickly or slowly to atmospheric temperature, and (3) reheating the tool to about 640 deg. for five minutes (in a lead bath) followed by cooling in air.

As at present conducted, the heat treatment of high-speed steel generally consists in heating the steel slowly to some 850 to 900 deg. C. and then as quickly as possible to some 1300 deg. C. The steel is then quenched in oil or in a molten salt bath of suitable composition, followed by reheating in an oil bath at a temperature of 500 to 600 deg. C., when it acquires "secondary hardness."

The increase of hardness resulting from reheating high-speed steel, after the high-

Fig. 312. — High-speed steel. Typical structure after annealing. Magnified 150 diameters. (Edwards.)

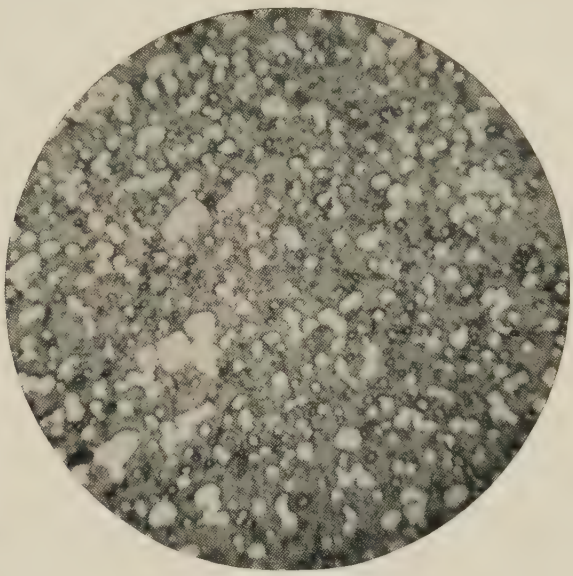


Fig. 313. — High-speed steel. Annealed at 780 deg. C. Magnified 1500 diameters. Tungsten 18.36 per cent. Chromium 4.05 per cent. Vanadium 1.04 per cent. Carbon 0.59 per cent. (J. V. Emmons.)

heat treatment, frequently called "secondary hardness," is the greater the higher the temperature from which the steel had been air or oil quenched.

High-quenching temperature also requires higher reheating temperature.

High-speed steel may be softened by prolonged heating at 800 to 900 deg. C. followed by very slow cooling.

The Brinell hardness of annealed high-speed steel is about 250, and after oil quenching from 1200 to 1300 deg. C., about 650.

The hardness of a tool is not an indication of its cutting properties, which rather depend upon its ability to retain its hardness, or indeed to acquire greater hardness when heated by friction to increasingly high temperatures. A very great hardness at the start, quickly lost at a relatively low temperature, is of little avail for high-speed cutting. Cutting hardness may be said to be chiefly dependent upon the stability of the solid solutions resulting from a suitable heat treatment.

It is probably true that the higher the temperature needed to cause the absorption of the carbides, the more stable will be the resulting solid solution retained at room temperature by air or more rapid cooling as the case may be, and also that the slower the rate of cooling sufficient to retain the solid solution at room temperature the more stable that solution.

The extraordinary stability of high-speed steel, then, or, which is the same thing,

its resistance to tempering, would be due to the very high temperature needed to form a solid solution with the existing carbides and to the relatively slow rate of cooling sufficient to retain that solution at room temperature.

As supporting the view that heat-treated high-speed steel is austenitic, we have the polyhedral character of its structure and the fact that it hardens on reheating to some 600 deg. C., the structure becoming more martensitic in appearance, this phenomenon being satisfactorily explained on the assumption that it results from the transformation of austenite.

In favor of the claim that heat-treated high-speed steel is martensitic, we have the fact that it is magnetic and also that a marked critical point occurs at some 300 deg. C. In view of the presence of that point, it is difficult to maintain that the steel is austenitic, that is untransformed, and if it does transform, it seems as if it must be into martensite, seeing that the point occurs precisely at the temperature when in the rapid cooling of carbon steel or in the slower cooling of some alloy steels martensite is formed, namely, the A″r temperature. Some believe that while high-speed steel is austenitic, after rapid cooling from a high temperature it is converted into martensite at about 600 deg. C., from which it would naturally follow that when in use the cutting edge of the tool, if austenitic at the start, is converted into martensite when heated by friction to that temperature. These views are confirmed by microscopical examination. This increase of hardness resulting from reheating rapidly cooled high-speed steel by friction or otherwise is sometimes called, as already noted, "secondary hardness."

M. A. Grossman believes that high-speed steel cooled from a high temperature contains martensite, and that on tempering additional martensite is formed, — the cutting hardness of the steel resulting from the presence of this second formation of martensite, which is more stable than the one produced by the high-temperature treatment.

Carbon steel tools, on the contrary, martensitic at the start, become troostitic at some 300 deg. C., and sorbitic at some 500 deg. C., hence lose their hardness.

Following this argument, manganese steel would probably be an excellent high-speed steel were it possible to cut at such high speed that the edge of the tool would be heated to a temperature high enough to convert it into martensite. In other words, the austenite in quenched manganese steel is too stable to permit its transformation into martensite by the heat generated in cutting, hence it does not acquire the necessary hardness.

The etching of high-speed steel was carefully investigated in the author's laboratory by Mr. M. Yatsevitch and the following conclusions appear warranted.

Alcoholic solution of picric and nitric acid may be used for etching high-speed steel, at times with satisfactory results. Picric acid should be in the form of a saturated solution in alcohol and its action may be intensified by the addition of some 20 per cent of water. In the absence of water, picric acid acts very slowly, the needed time of etching moreover increasing rapidly as the temperature from which the steel cools increases and as the speed of cooling increases, in other words as the conditions of the industrial treatment of high-speed steel are approached. Picric-acid etching is satisfactory for steel in the annealed condition, as shown in Figure 314, where the bright particles of carbide are clearly revealed embedded in a dark matrix. The time of etching was 6 minutes. The same steel after high-heat treatment could not be etched by picric acid even after a 48-hour immersion.

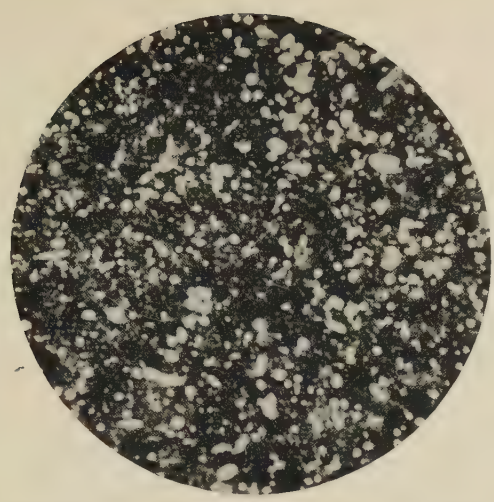


Fig. 314. — Annealed. Etched with picric acid six minutes.

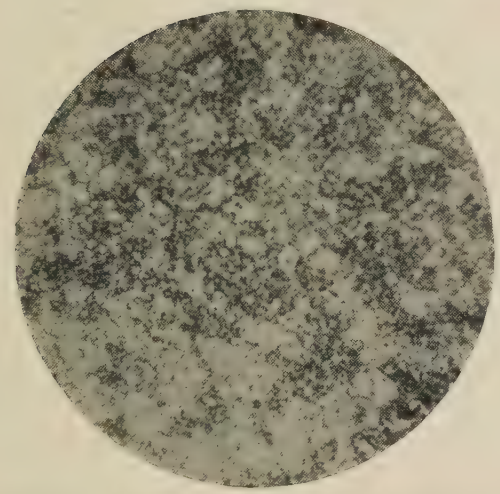


Fig. 315. — Annealed. Etched with nitric acid two minutes.

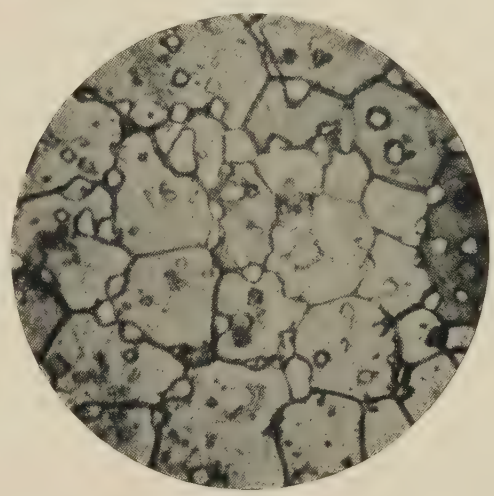


Fig. 316. — Heated to 1200 deg. C. and quickly cooled. Etched with nitric acid fourteen minutes.

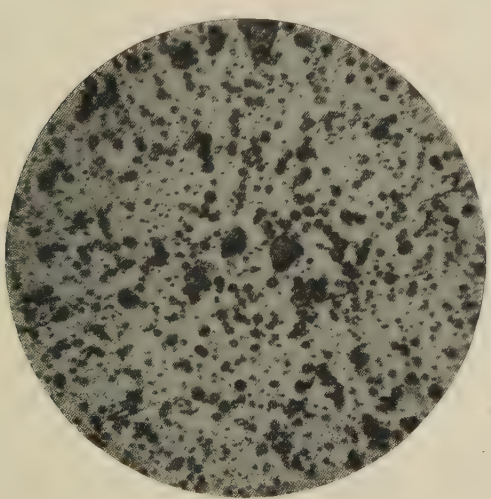


Fig. 317. — Annealed. Etched with hydrogen peroxide and sodium hydrate.

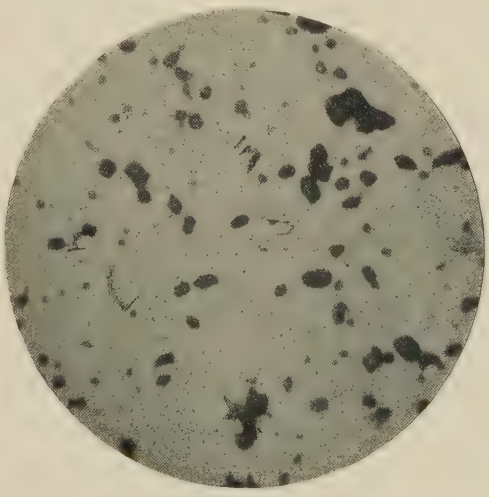


Fig. 318. — Heated to 1240 deg. C and quickly cooled. Etched with hydrogen peroxide and sodium hydrate.

High-speed steel. Tungsten 18.20 per cent, chromium 3 per cent, vanadium 0.95 per cent, carbon 0.62 per cent, silicon 0.27 per cent, manganese 0.38 per cent. All photomicrographs are magnified 980 diameters. (M. Yatsevitch, in the author's laboratory.)

Nitric acid in alcohol (some 10 per cent acid) is less satisfactory for etching annealed specimens (Fig. 315) but much more effective in revealing the structure of heat-treated specimens (Fig. 316). Its action while much more rapid than that of picric acid, also becomes decidedly slower as the temperature reached on heating and as the speed of cooling increase, and therefore as the mineralogical hardness of the steel increases. The annealed specimen shown in Figure 315 was etched for 2 minutes while after high-heat treatment (Fig. 316) an immersion of 14 minutes was required. It will be observed that both picric and nitric acid etching leave the free carbides bright while darkening the matrix, and that nitric acid readily reveals the polyhedral

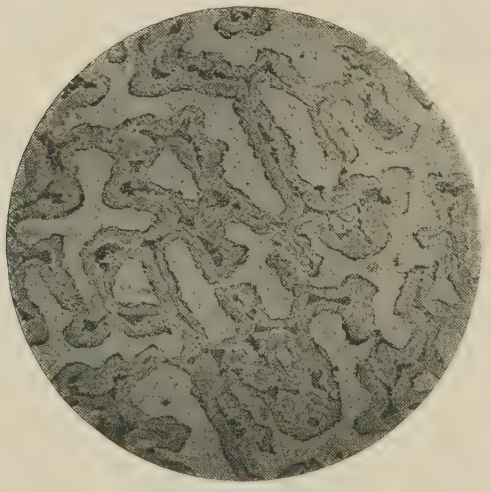


Fig. 319. — Magnified 86 diameters.

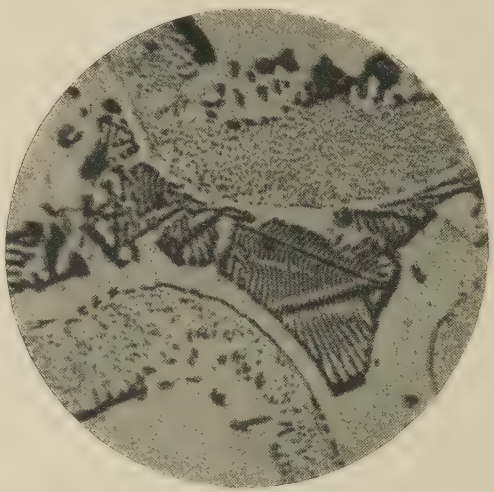


Fig. 320. — Magnified 980 diameters.

High-speed steel. Cast. Etched with hydrogen peroxide and sodium hydrate. (M. Yatsevitch, in the author's laboratory.)

structure of heat-treated samples. It is also apparent that the length of time needed to develop the structure of high-speed steel is an indication of the heat treatment it has received. Obviously, increasing temperature and speed of cooling produce in the matrix of high-speed steel changes which are not brought out in the etched structure of the metal but which are made apparent by a much greater resistance to the action of picric and nitric acid and also by increased mineralogical hardness.

Mr. Yatsevitch has obtained interesting and valuable results in using for etching high-speed steel a solution of hydrogen peroxide and sodium hydrate. This reagent etches the particles of free carbide *dark* while leaving the matrix white and brilliant even after prolonged immersion (Figs. 317 and 318). The etching time (about 10 to 15 minutes) remains the same regardless of the heat treatment applied. The method affords a sure means of revealing the existence of the free carbide to the exclusion of everything else. It does not reveal the polyhedral structure of the steel after high-heat treatment, clearly because the net surrounding the grains does not indicate the presence around them of membranes of free carbide.

The cast structure of the high-speed steel used in these experiments is illustrated in Figures 319 and 320. It may be safely inferred that the constituent colored dark by the Yatsevitch reagent is the carbide and that the latter forms a component, therefore, of the eutectic or eutectoid evidently present in the cast metal.

Cobalt Steel. It is claimed that the influence of cobalt is similar to that of nickel, increasing strength and elastic limit with relatively little loss of ductility, that the presence of 34.5 per cent cobalt in iron increases the saturation value 10 to 13 per cent, that at high induction the permeability may be 25 per cent higher than that of pure iron, that cobalt steel has higher coercive force than tungsten steel for permanent magnets. Professor Honda has described a cobalt steel containing 35 per cent cobalt which is said to be far superior to ordinary magnet steel. The high price of cobalt generally renders the cost of these cobalt steels prohibitive.

CHAPTER XXI

CAST IRON

Cast iron differs sharply from steel in being deprived of malleability. This lack of malleability is due to the presence of a large quantity of carbon, generally between 2.50 and 4.00 per cent. The carbon present in cast iron may be (1) wholly in the graphitic condition, (2) wholly in the combined condition, and (3) partly in the graphitic and partly in the combined condition. These three types of cast iron should be separately considered. The solubility of carbon in iron and the factors influencing the formation of graphite or of combined carbon should, however, first be noted.

Solubility of Carbon in Iron. — Slightly above its melting point (1530 deg. C.) pure iron does not appear to be able to dissolve more than some 5 per cent carbon. As its temperature increases, however, its saturation point for carbon increases materially.

Results obtained by Ruff and Goecke and by Hanemann are shown graphically in Figure 321. Hanemann's results are indicated by crosses. Since the carbide Fe_3C or cementite contains 6.67 per cent carbon, it may be inferred from the results tabulated above, (1) that iron-carbon alloys saturated with carbon consist between 1130 (the melting point of the eutectic as later explained) and 1823 deg. of liquid solutions of iron and Fe_3C, the proportion of the latter constituent increasing with the temperature, and (2) that at 1823 the alloy is liquid Fe_3C. From the fact that the amount of carbon dissolved at 2220 deg. C., namely 9.60 per cent, is the amount called for by the carbide Fe_2C it is further inferred (1) that between 1823 and 2220 deg. the alloys are liquid solutions of Fe_3C and Fe_2C, the latter increasing and the former decreasing with the temperature, and (2) that at 2220 deg. the alloy is liquid Fe_2C. At higher temperature some of the Fe_2C breaks up into iron and graphite (Fe_2C = 2 Fe + C), the resulting graphite floating to the top of the liquid bath, thus explaining the smaller and decreasing proportions of dissolved carbon at temperatures exceeding 2220 deg. The break in the curve at 1823 (Fig. 321) corresponds to the formation of Fe_3C, the break at 2220 deg. to the formation of Fe_2C. Taking iron with its maximum proportion of carbon, namely at 2220 deg., when it is capable of dissolving 9.60 per cent carbon, as previously stated, it then consists of liquid Fe_2C. On cooling it is not capable of retaining so much carbon, some of it being rejected as graphite through the transformation of some of the Fe_2C into Fe_3C and graphite ($3\ Fe_2C = 2\ Fe_3C + C$). This formation of Fe_3C at the expense of Fe_2C with rejection of graphite continues until at 1823 deg. Fe_3C only is present (6.67 per cent carbon). On further cooling the alloy must continue to reject carbon, now through the transformation of some of the Fe_3C into iron and graphite ($Fe_3C = 3\ Fe + C$), a

transformation which continues until a temperature of 1130 deg. is reached, when the alloy contains 4.30 per cent carbon and when further cooling now causes its

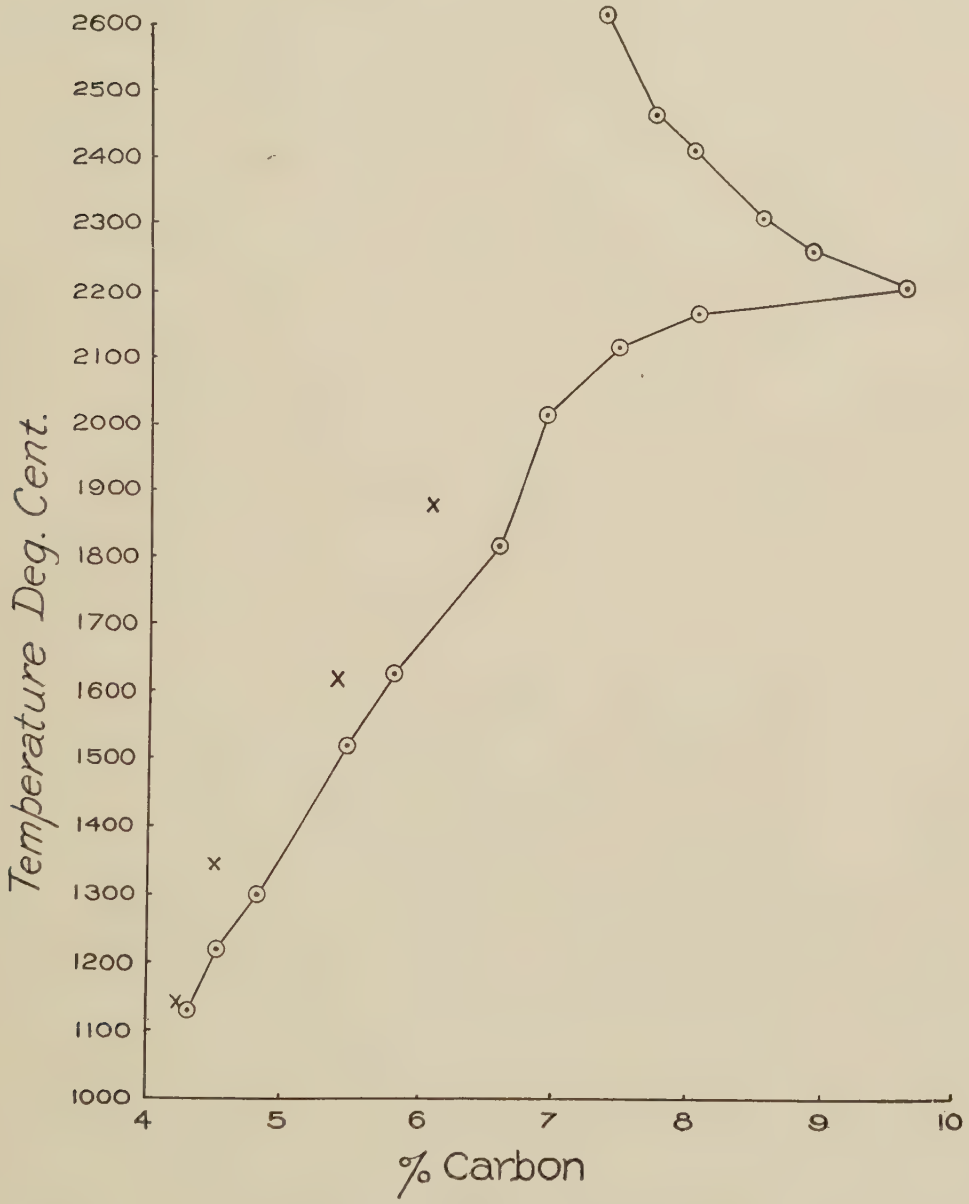


Fig. 321. — Solubility of carbon in iron.

solidification. The possibility of the carbide Fe_3C solidifying out of the liquid solution being later converted wholly or in part into iron and graphite will be considered in the following pages.

Formation of Combined and Graphitic Carbon. — It will be explained in Chapter

XXV that when cast iron solidifies the carbon probably remains in the combined condition and that the resulting carbide, Fe_3C, is partly free and partly in solid solution in the iron. This Fe_3C, however, is an unstable compound and when formed at a high temperature it is readily decomposed into graphite and iron according to the reaction

$$Fe_3C = 3\ Fe + C$$

hence the formation of graphitic carbon in cast iron. Two factors are conspicuous in promoting the formation of graphitic carbon, (1) a slow rate of cooling through and below the solidification period and (2) the presence of silicon. The gray, i.e. graphitic, cast irons are generally those which have been cast in sand and hence slowly cooled and which contain a relatively large percentage of silicon. It follows that under otherwise identical conditions and compositions a large casting will become more graphitic on solidifying than a smaller one since it will cool more slowly; also that of two castings of equal size, cooled under like conditions and of identical composition except as to their silicon contents, the one richer in silicon will contain more graphitic carbon. The conditions most effective in preventing the formation of graphitic carbon and in promoting, therefore, the retention of carbon in its combined form are (1) quick rate of cooling through and below the solidification range and (2) the presence of much sulphur or manganese and little silicon.

Cast Iron Containing only Graphitic Carbon. — Cast irons containing a considerable amount of graphitic carbon are known as gray cast irons because of the appearance of their fracture, which is grayish or blackish and coarsely crystalline. Cast irons containing the whole of their carbon in the graphitic condition and therefore free from combined carbon are extreme types seldom produced. Their structure, however, should be considered.

Proceeding as we did in the case of steel we shall first assume cast iron to be a pure alloy of iron and carbon, free, therefore, from its usual impurities. If the whole of the carbon is in the graphitic condition it is evident that cast iron can only contain the two constituents graphite and iron or ferrite. We may therefore anticipate its structure. It will, however, be interesting to study the mode of occurrence of the graphitic carbon. The structure of cast iron practically free from combined carbon is illustrated both before and after etching in Figures 322 and 323. The metal will be seen to consist of an iron or ferrite matrix in which are embedded many irregular and generally elongated and curved plates of graphite. These graphite plates break up so effectively the continuity of the metallic mass as completely to destroy the ductility and malleability of a substance (ferrite) by nature very ductile and malleable. The brittleness of high graphitic cast iron is not due so much to the brittleness of the graphite it contains, nor even to its large proportion of graphite, as to the thorough manner in which the continuity of its otherwise ductile matrix is destroyed by the shape and distribution of the graphite particles.

It will be seen in another chapter that when the graphite occurs in small rounded particles as it does in malleable cast iron the ferrite matrix may retain considerable ductility and malleability.

The ferrite matrix of this highly graphitic cast iron (Fig. 323) will be seen to be made up, after etching, of the polyhedral crystalline grains characteristic of carbonless iron, the ferrite of cast iron being similar in this and other respects to the ferrite of wrought iron and of hypo-eutectoid steel. In impure cast iron it undoubtedly holds in solution silicon and possibly, to some extent, other impurities.

Fig. 322. — Gray cast iron free from combined carbon. Magnified 100 diameters. Not etched. (F. C. Langenberg, in the author's laboratory.)

Fig. 323. — Same metal as in Figure 322. Magnified 100 diameters. Etched. (F. C. Langenberg, in the author's laboratory.)

Highly graphitic cast iron is brittle and deprived of ductility and malleability because of the presence of numerous plates of graphitic carbon; it is weak because of the presence of graphite plates and because of the relative weakness of its matrix; it is soft and therefore easily machined because of the softness both of its matrix and of the graphite it contains; it expands on solidifying because of the formation, with increase of bulk, during solidification of a large amount of graphitic carbon. It should be noted that because of its low specific gravity graphite will occupy a relatively large proportion of the bulk of the metal. Cast iron, for instance, containing by weight 3 per cent of graphite contains by volume some 12 per cent of that element.

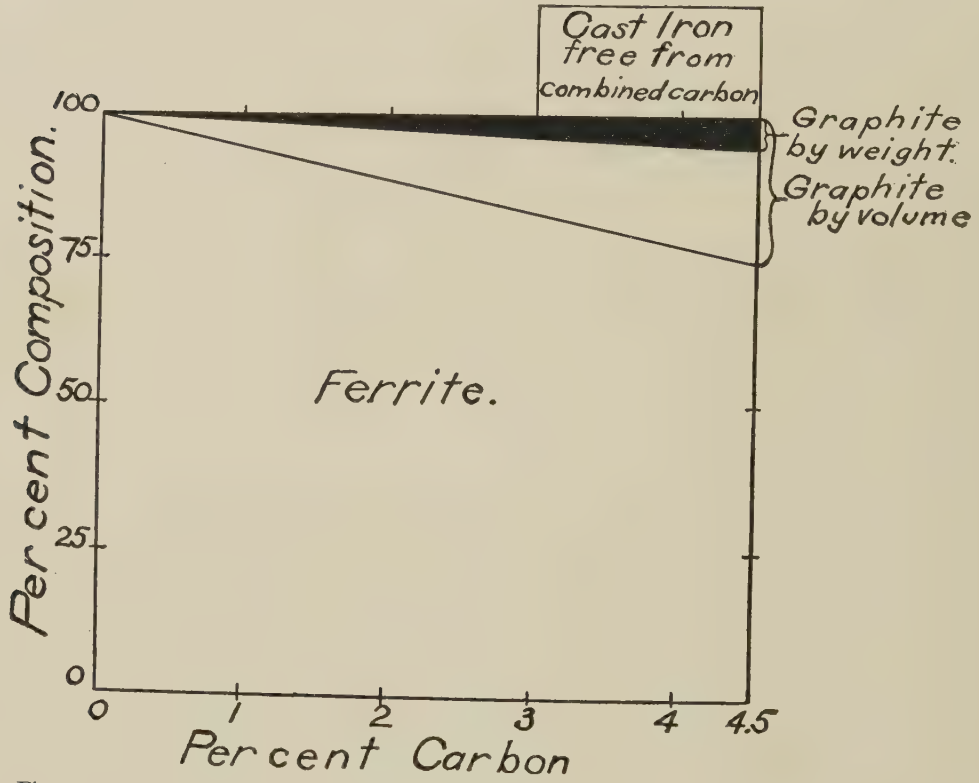


Fig. 324. — Structural composition diagram of iron-carbon alloys free from combined carbon.

As might be expected the rate of solidification and further cooling has some influence both upon the shape and size of the graphite particles as well as upon the size of the ferrite grains, and therefore upon the physical properties of the metal, very slow solidification promoting the formation of large graphite plates and of large ferrite grains. Were it possible to cause the graphite in cast iron to occur in small rounded particles instead of sharp, curved plates, its ductility and strength would undoubtedly be greatly increased.

The diagram of Figure 324 shows graphically the structural composition of iron-carbon alloys in which the whole of the carbon occurs as graphite. Only those alloys, however, containing from 3 to 4.5 per cent carbon can be produced. Indeed in the absence of silicon even these are quite unobtainable. With less than 3 per cent carbon it is well-nigh impossible to prevent the retention of some combined carbon,

while with less than 2 or at least with less than 1.50 per cent carbon the whole of the carbon is likely to be in the combined condition. The diagram, therefore, is only a theoretical one. It has, nevertheless, its interest, for it will be shown in another chapter to represent the stable and final equilibrium of the iron-carbon system. The percentage of graphite by volume has also been indicated.

Cast Iron Containing only Combined Carbon. — Cast iron containing only combined carbon and free, therefore, from graphitic carbon, is called "white" cast iron from the aspect of its fracture, which is white, brilliant, and highly metallic. The

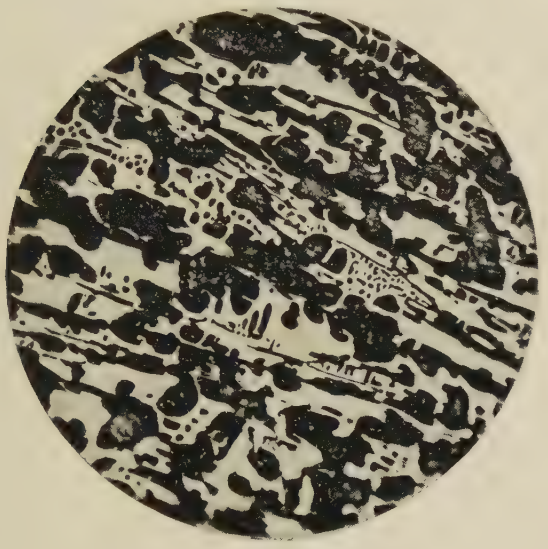


Fig. 325. — White cast iron. Magnified 56 diameters.

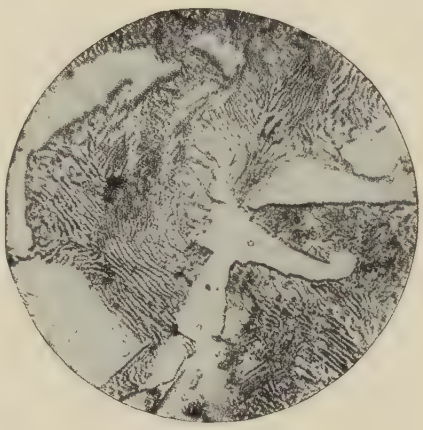


Fig. 326. — White cast iron. Magnified 500 diameters. (Wüst.)

absence of graphitic carbon is generally due (1) to the presence of much manganese and sulphur and of little silicon, (2) to quick cooling through and below the solidification period, or (3) to both low silicon, high manganese and sulphur, and quick solidification. Cast iron, for instance, may contain so much sulphur and manganese and so little silicon as to be white even after slow solidification, or it may solidify so quickly as to be white even in the presence of much silicon and little manganese and sulphur.

A familiar instance of the marked influence of the rate of cooling is afforded by the casting in the metal molds of casting machines of cast iron which if cast in sand would have been gray, whereas it is now white. Small castings, since they cool more quickly, become white more readily than larger ones.

In the absence of graphitic carbon the structure of cast iron should resemble the structure of a very high carbon steel, i.e. it should consist after slow cooling of pearlite and of a large amount of free cementite. This is found to be the case, as shown in Figure 325, in which is illustrated the structure of white iron containing about 3 per cent of combined carbon. Theoretically this alloy should contain nearly 66 per cent of pearlite and 34 per cent of free cementite. The dark constituent in the photograph is pearlite, the light one, visibly in relief, cementite. The structure of white cast iron is also shown in Figure 326 under high magnification, the laminations of pearlite being clearly seen. The structure of white cast iron is further illustrated in Figures

327 and 328 after Guillet. These photomicrographs are reproduced here because they afford an interesting example of the action of sodium picrate in coloring free cementite while leaving pearlite uncolored.

The structural composition of white cast iron is to be calculated like the composition of any hyper-eutectoid steel of known carbon content, as explained in Chapter V, the following relation existing between the percentage of pearlite and that of carbon in the iron, on the assumption that pearlite contains 0.85 per cent carbon:

$$P = 115 - 17\ C$$

the balance of the metal being of course free cementite. While structurally it resembles high carbon steel, white cast iron is deprived of malleability, being indeed

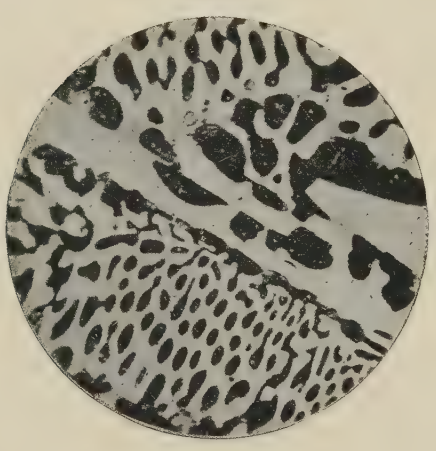


Fig. 327. — White cast iron. Magnified 200 diameters. Etched with picric acid. (Guillet.)

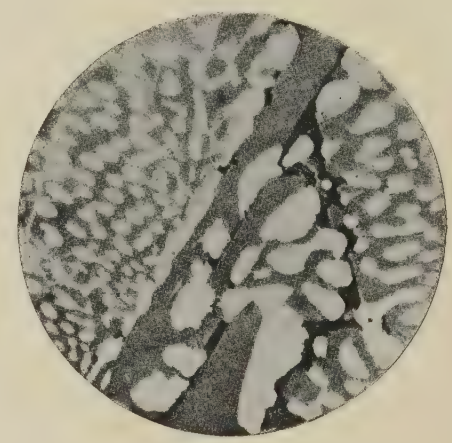


Fig. 328. — Same metal as in Fig. 327. Magnified 200 diameters. Etched with sodium picrate. (Guillet.)

very brittle and very hard. This brittleness and hardness are due to the very large proportion of free cementite present, which itself is very hard and brittle.

It will be evident that, starting from carbonless iron, as the carbon increases, at first low carbon steel is produced and then in succession medium high carbon steel, high carbon steel, and finally white cast iron, each metal passing gradually into the next without any sharp line of demarcation between them. It is logical to base the distinction between high carbon steel and white cast iron upon the malleability of the former and the non-malleability of the latter and this is altogether a question of carbon content. The dividing line may be drawn somewhat arbitrarily at 2 per cent carbon, or following the equilibrium diagram (Chapter XXV) at 1.70 per cent. As a matter of fact steels are very seldom manufactured containing more than 1.70 per cent carbon, while white cast iron rarely contains less than 2.25 per cent carbon. Between the steel series, therefore, and the white cast-iron series there is a natural gap, the existence of which generally removes any doubt as to the nature of the metal under examination.

The diagram of Figure 329 indicates graphically the structural composition both proximate and ultimate of any iron-carbon alloy containing from 0 to 6.67 per cent combined carbon, that is, from 100 per cent ferrite to 100 per cent cementite.

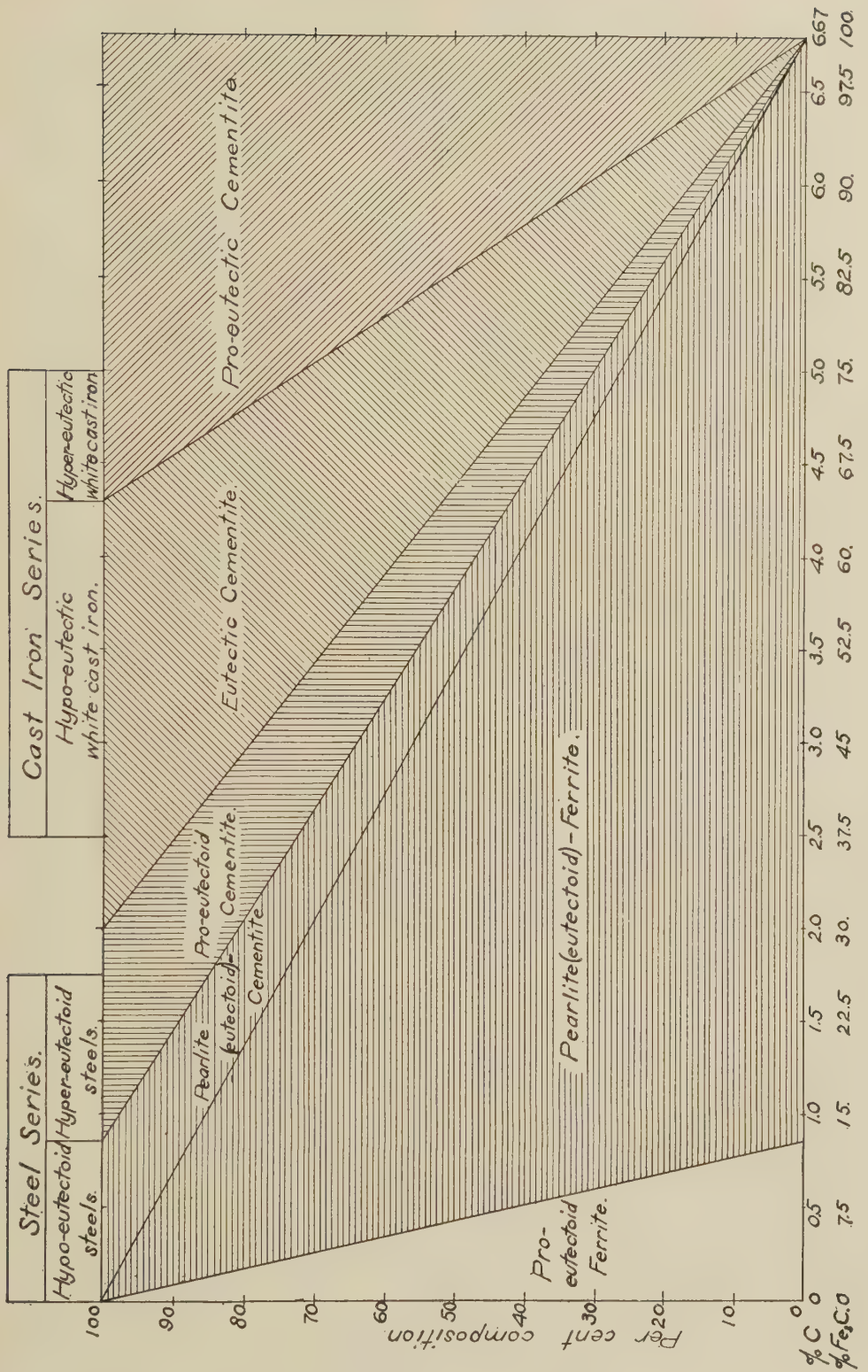


Fig. 329. — Structural composition diagram of iron-carbon alloys free from graphite carbon.

It will be noted that two sources of ferrite are indicated in the diagram, namely, (1) pearlite (eutectoid) ferrite and (2) pro-eutectoid or free ferrite, the sum of both being known as total ferrite, while four sources of cementite are to be considered, namely, (1) pearlite (eutectoid) cementite, (2) pro-eutectoid cementite, (3) eutectic cementite, and (4) pro-eutectic cementite, the sum of all four being known as total cementite and that of (2), (3), and (4) as free cementite. Let us recall the meaning of these terms:

Pearlite or eutectoid ferrite is the ferrite included in pearlite.

Free or pro-eutectoid ferrite is the ferrite liberated as hypo-eutectoid steel cools slowly from its upper critical point (Ar_3 or $Ar_{3\cdot2}$) to its lower point (Ar_1).

Pearlite or eutectoid cementite is the cementite included in pearlite.

Pro-eutectoid cementite is the cementite that is liberated as hyper-eutectoid metal cools slowly from its upper critical point (Ar_{cm}) to its lower point ($Ar_{3\cdot2\cdot1}$).

Eutectic cementite is the cementite included in the austenite-cementite eutectic which forms at the end of the solidification of alloys containing more than some 1.70 per cent carbon, as explained in Chapter XXV.

Pro-eutectic cementite is the cementite which forms between the beginning and the end of the solidification of alloys containing more than 4.3 per cent carbon, as explained in Chapter XXV. Howe calls it "primary" cementite.[1]

The portions of the diagram corresponding respectively to the steel series and to the white cast-iron series have also been indicated, leaving two groups of alloys unrepresented by industrial products, namely, those containing between 1.70 per cent and 2.25 per cent carbon and those containing more than 5 per cent of carbon.[2] The steel portion of this diagram has been used in Chapter V.

Cast Iron Containing both Combined and Graphitic Carbon. — Cast-iron castings nearly always contain both combined and graphitic carbon. In the majority of cases they contain from 0.25 to 1.50 per cent of combined carbon, the balance of that element being in the graphitic condition. The chief factors affecting this distribution of carbon between the combined and the graphitic states have already been alluded to; they are (1) the rate of cooling during and below solidification (hence the size of the castings) and (2) the presence of silicon, manganese, and sulphur, the first element promoting, and the last two opposing, the formation of graphitic carbon. If it be considered (1) that graphitic carbon is soft, (2) that the presence of much graphite, since it implies little combined carbon, means the occurrence of soft ferrite in the cast iron, (3) that combined carbon (cementite) is very hard, and (4) as later explained, that the presence of combined carbon, at least up to a certain proportion, greatly increases the strength of cast iron, it will be evident that the physical properties of cast iron, especially its strength and hardness, will depend chiefly upon the proportion of combined and graphitic carbon it contains.

[1] Howe questions the actual existence of commercial hyper-eutectic white cast iron on the ground that pro-eutectic cementite, as later explained, is so rapidly converted into graphite that it cannot be retained unless indeed by extremely quick cooling or in the presence of much manganese.

[2] It should be remembered that we are considering here pure alloys of iron and carbon. In the presence of much manganese (or chromium) iron may contain as much as 6.50 per cent and even much more carbon, while in their absence cast iron very seldom contains more than 4.5 per cent carbon. Again some products are offered for sale under the name of semi-steel which may contain between 1.70 and 2.50 per cent of total carbon entirely combined, forming, therefore, a sort of connecting link between the steel and the cast-iron series. They are frequently obtained by remelting cast iron in cupola furnaces in the presence of considerable iron or steel scrap. Washed metal likewise may contain between 1.70 and 2.50 per cent of total and entirely combined carbon but this is a semi-finished product resulting from a partial refining only of cast iron.

Let us first consider the structure of cast iron containing a small amount, say 0.25 per cent, of combined carbon and some 3 per cent of graphitic carbon (Fig. 330). The combined carbon will yield 15 times its own weight of cementite ($0.25 \times 15 = 3.75$ per cent) and the resulting cementite 7.8 times its own weight of pearlite ($3.75 \times 7.8 = 29.25$ per cent), or more quickly,

$$0.25 \times 117 = 29.25 \text{ per cent pearlite}$$

exactly as in the case of steel.

The cast iron under consideration will therefore contain 29.25 per cent pearlite, 3 per cent graphite, and the balance, 67.75 per cent, necessarily free ferrite. Cast

Fig. 330. — Gray cast iron. Hypo-eutectoid matrix (0.25 per cent combined carbon). Magnified 100 diameters. (Boylston.)

iron containing graphitic carbon may be considered as being made up of two distinct parts, namely, (1) graphite and (2) a metallic matrix in which the graphite particles are embedded. It will be obvious, moreover, that the metallic matrix of gray cast iron is in reality a steel matrix, since it necessarily consists, like steel, of an aggregate of ferrite and cementite partly associated to form pearlite. In cast iron free from combined carbon the matrix is pure ferrite; with a little combined carbon it is of the nature of a low carbon steel; as the combined carbon increases the metallic matrix is converted into steel of increasing carbon content; with less than some 0.80 per cent carbon the matrix resembles a hypo-eutectoid steel; with some 0.80 per cent carbon the matrix is pure pearlite, i.e. eutectoid steel; with more than 0.80 per cent carbon some free cementite is formed, the matrix consisting of hyper-eutectoid steel. In other words, as the proportion of combined carbon increases, structural changes take place in the metallic matrix of cast iron identical to those observed and described in the case of steel. The structure of cast iron containing increasing proportions of combined carbon is illustrated in Figures 330 to 332.

The foregoing considerations justify us in considering gray cast iron as steel, that is as an aggregate of ferrite and cementite, the continuity of which is destroyed by

the presence of numerous graphite plates, the enormous difference in properties between gray cast iron and steel being due solely to the presence of this graphitic carbon, or rather to the breaking of the continuity of the mass which it implies. To illustrate further, if it were possible to remove bodily from a chunk of cast iron every particle of graphite, its strength and ductility would not probably be greatly increased because its continuity would still be effectively destroyed by the empty spaces once occupied

Fig. 331. — Gray cast iron. Eutectoid matrix. Magnified 500 diameters. (E. L. Reed, in the author's laboratory.)

Fig. 332. — Gray cast iron. Hyper-eutectoid matrix. Magnified 500 diameters. (Wüst.)

by graphite. If not too high in carbon, however, it would now be weldable and could be forged into a small piece of steel, or it could be remelted and cast into a sound steel casting.

Mottled Cast Iron. — Cast irons are sometimes produced that are partly gray and partly white, that is, made up of particles containing graphitic carbon and of particles free from graphite. Their structure is well shown in Figure 333. They are called "mottled" because of the appearance of their fracture.

Structural Composition of Cast Iron. — The structural composition of any cast iron of known percentages of graphitic and combined carbon considered as a pure alloy of iron and carbon can readily be calculated by following the method employed in the case of steel. In order that cast iron may have a matrix of eutectoid composition it must be free from both excess ferrite and excess cementite, that is, it must contain ferrite and cementite in the exact proportion of 1 part of cementite to 6.8 parts of ferrite. If the cast iron contains G per cent of graphite and C per cent of combined carbon forming $15 \times C$ per cent of cementite, the balance of the metal, $100 - G - 15\ C$, will be ferrite. Consequently if

$$100 - G - 15\ C = 6.8 \times 15\ C = 102\ C$$

or if

$$100 - G - 117\ C = 0$$

the matrix will contain pearlite only; if $100 - G - 117\ C$ is greater than 0 the matrix will be hypo-eutectoid; if $100 - G - 117\ C$ is smaller than 0 the matrix will be hyper-eutectoid. In the presence of 3 per cent graphite, for instance, the follow-

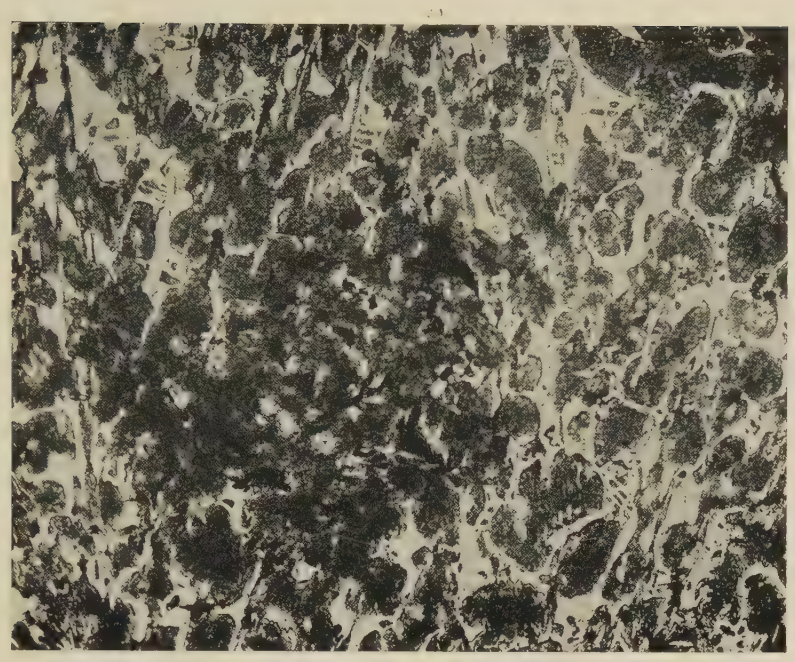


Fig. 333. — Mottled iron. Magnified 100 diameters. (Boylston.)

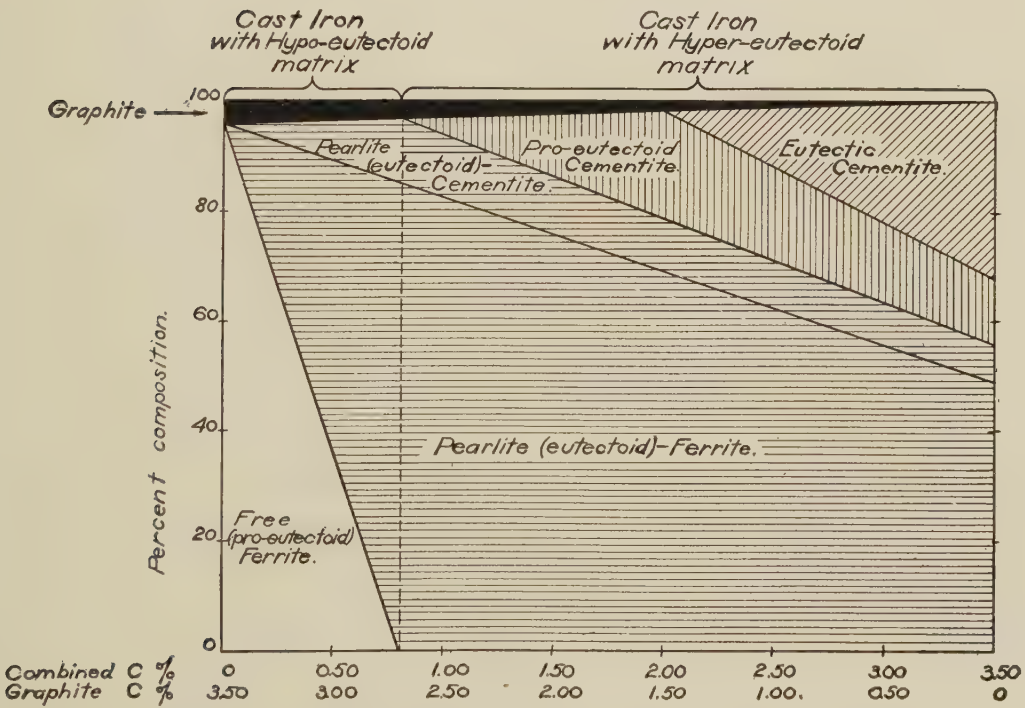


Fig. 334. — Structural composition diagram of iron-carbon alloys containing a constant proportion of total carbon (3.50 per cent), but varying percentages of combined carbon (from 0 to 3.50 per cent).

ing relation will indicate the needed percentage of combined carbon to make the matrix entirely pearlitic:

$$100 - 3 - 117\ C = 0$$

which gives for C very nearly 0.83 per cent.

It will be sufficiently accurate to assume in every case that gray cast iron containing less than 0.85 per cent combined carbon has a hypo-eutectoid matrix while cast iron containing more combined carbon has a hyper-eutectoid matrix.

In calculating the structural composition of cast iron two cases, then, should be considered: (1) the cast iron contains less than 0.85 per cent combined carbon; it has a hypo-eutectoid matrix, and (2) it contains more than 0.85 per cent combined carbon; it has a hyper-eutectoid matrix. In the first instance we have the following relations between the percentage of graphitic carbon, G, the percentage of combined carbon, C, the percentage of ferrite, F, and the percentage of pearlite, P:

$$(1)\ F + P + G = 100$$
$$(2)\ P = 7.8 \times 15\ C = 117\ C$$

If C = 0.50 per cent, for instance, and G = 3 per cent, the iron would contain 58.50 per cent pearlite, 38.50 per cent ferrite, and 3 per cent graphite.

If the iron has a hyper-eutectoid matrix, that is, if it contains more than 0.85 per cent of combined carbon, we can write the following equations, Cm representing the percentage of free cementite:

$$(1)\ P + Cm + G = 100$$
$$(2)\ P = \frac{7.8}{6.8} F = \frac{7.8}{6.8} (100 - G - 15\ C)$$

or

$$P = 1.15\ (100 - G - 15\ C)$$

the second equation expressing the fact that the totality of the ferrite $(100 - G - 15\ C)$ is included in the pearlite and that the percentage of pearlite is equal to $\frac{7.8}{6.8}$ times that of ferrite. If cast iron contains 2 per cent of graphite and 1.25 per cent of combined carbon, for instance, the foregoing equations indicate the following structural composition: pearlite 91.14 per cent, free cementite 6.86 per cent, and graphite 2 per cent.

The structural, graphical diagram of cast iron containing both combined and graphitic carbon has been constructed in Figure 334 in accordance with the scheme followed in these chapters. It is assumed in this diagram that the total carbon remains constant at 3.50 per cent and that the amount of combined carbon increases from 0 to 3.50 per cent, in this way including the two extreme cases corresponding respectively to absence of combined carbon and of graphitic carbon. If this diagram be compared with that of the structural composition of steel, Chapter V, the steel nature of the metallic matrix of cast iron will be apparent. It will be noted that in the present diagram when the proportion of combined carbon exceeds 1.7 per cent there are two sources of free cementite indicated, namely, pro-eutectoid cementite and eutectic cementite; the origin of the latter will be made clear in Chapter XXV. Both of these cementites constitute the free cementite present in cast iron containing more than 1.7 per cent of combined carbon; while formed, as later explained, at different periods of the cooling, they appear to coagulate together and cannot be distinguished form each other under the microscope.

Physical Properties of Cast Iron vs. Its Structural Composition. — The physical properties of cast iron must necessarily depend to a very great extent upon the properties of its steel matrix, from which it follows that its hardness and strength will increase with increasing combined carbon, the hardness indefinitely, the strength up to the eutectoid carbon ratio. It is evident, therefore, that cast iron of maximum strength (1) should have a steel matrix of maximum strength, i.e. should contain in the vicinity of 0.85 per cent combined carbon and (2) should contain as little graphitic carbon as possible since every graphite particle is a source of weakness; in other words, the nearer cast iron approaches a steel of maximum strength the greater will be its strength. After having secured the desired amount of combined carbon to give strength it is evident that a reduction of the graphitic carbon must mean a corresponding reduction of the total carbon in cast iron. In ordinary cupola practice for the production of cast-iron castings, however, which consists in remelting pig iron of suitable composition, the proportion of total carbon is difficult to control, being necessarily between 3 and 4 per cent, and we must depend to produce strength almost altogether upon the retention in the combined condition of a suitable proportion of carbon. The total carbon may be decreased, however, by the use of iron and steel scrap as part of the burden of the cupola, resulting in increased strength for same percentage of combined carbon, or by remelting in a so-called "air furnace," i.e. under oxidizing conditions when part of the carbon is burnt out. These low total carbon, and therefore tenacious, cast-iron castings are sometimes offered for sale under the name of semi-steels, a practice somewhat misleading, for they are not steel in any sense of the word since they are not malleable, have very little ductility, and generally contain a considerable amount of graphitic carbon.

If soft cast-iron castings are desired so that they may be easily machined, they should contain as little combined carbon as possible. In the presence of but little combined carbon, however, the iron will not be very tenacious, strength and softness being antagonistic. If the castings are to be hard they should contain much combined carbon and, therefore, little graphite. In extreme cases they will be free from graphite, when their hardness will be very great, but they will then also be very brittle. In the majority of cases castings are wanted soft enough to be easily machined and at the same time of fair strength. This combination of properties is evidently to be obtained by producing a matrix corresponding to a medium high carbon steel, i.e. by causing the cast iron to retain some 0.30 to 0.60 per cent of combined carbon.

The percentage of combined carbon in cast iron, upon which its physical properties primarily depend, can be ascertained more quickly and readily by microscopical examination than by chemical analysis and quite as accurately.

Chilled Cast-Iron Castings. — It is sometimes desired to produce cast-iron castings very hard near the outside but soft and relatively tough in the center. This may be done by so regulating the composition and solidification as to prevent the formation of graphite in those portions that should be hard while allowing it to form in the portions that should be soft. The means generally employed consist in using iron plates for those parts of the molds corresponding to the parts of the castings that are to be hard and sand for the other parts, the quicker solidification and further cooling of the metal coming in contact with the iron plates causing the retention of much combined carbon. The resulting castings are known as "chilled" castings. Important instances of the application of this method are to be found in the manufacture of chilled cast-iron wheels and of chilled rolls. It will be evident that the presence

of sulphur and manganese in the cast iron should promote the retention of combined carbon on quick cooling while the presence of silicon and of large percentages of total carbon should hinder it. The chemical composition of cast iron to be converted into chilled castings should therefore be carefully regulated. Microscopical examination should prove of much value in examining the depth and quality of "chills."

Cast Iron of Eutectic Composition. — The alloy of iron and carbon containing 4.30 per cent carbon has the lowest melting point (1130 deg. C.) of all alloys of that series and is consequently known as eutectic alloy. The nature of eutectic alloys will be made clear in Chapter XXIV. Those alloys solidify at a constant temperature, whereas the solidification of alloys containing more or less carbon than the eutectic ratio covers a range of temperature which increases in width as the com-

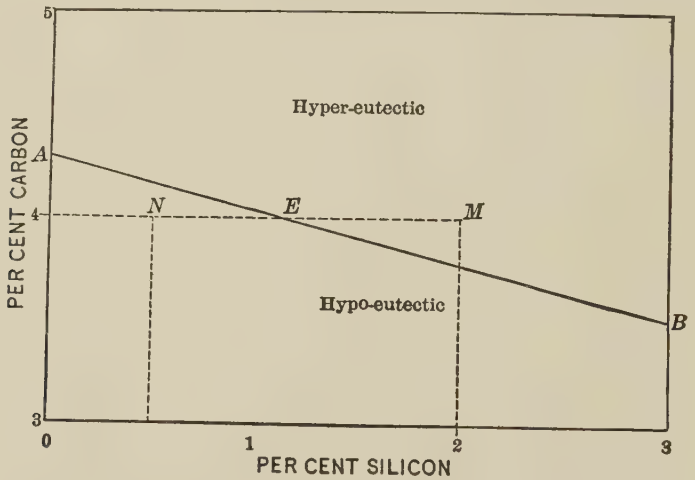


Fig. 335. — Influence of silicon-content on the percentage of carbon in the eutectic alloy.

position of the alloy is farther removed from that of the eutectic, as explained in Chapter XXV. In other words, eutectic alloys pass quickly from the liquid to the solid state while hypo- and hyper-eutectic alloys pass through a pasty or semi-fluid period which may be of considerable duration, a condition, as later explained, which must be favorable to the formation of large graphite particles.

Eutectic Cast Iron vs. Impurities. — While as stated in the preceding paragraph the eutectic point for pure alloys of iron and carbon corresponds to 4.30 per cent carbon, it is quite certain that some at least of the impurities always present in commercial cast iron affect in a marked degree the percentage of carbon needed to produce the eutectic alloy, i.e. the alloy of lowest melting point, generally reducing the needed amount of carbon. From the work of Wüst and Petersen, for instance, we are led to infer that the presence of 1 per cent of silicon lowers that carbon some 0.30 per cent. These authors' results may be profitably represented graphically as shown in Figure 335. The meaning of the diagram is obvious. The line AB divides cast iron into hyper- and hypo-eutectic metal according to its percentages of carbon and silicon. With 4 per cent of carbon and 2 per cent of silicon, for instance, the cast iron is hyper-eutectic, since its composition is represented by the point M in the hyper-eutectic range, while with the same amount of carbon but in the presence of only 0.5 per cent of silicon, the metal is hypo-eutectic, since its composition is represented by the point

N in the hypo-eutectic range; with 3 per cent silicon some 3.50 per cent carbon suffices to produce the eutectic alloy, etc.

The Strength of Cast Iron vs. the Size and Form of the Graphite Particles. — Attention has already been called to the fact that the strength of cast iron is not only affected by the amount of carbon present, but also and in a marked degree by the size and form of the graphite particles, long, curved plates of that constituent, for instance, being much more effective in reducing the strength than small rounded particles.

Eutectic Cast Iron vs. the Size and Form of the Graphite Particles. — It seems probable, as more fully explained in Chapter XXV, that the bulk of the graphite present in cast iron forms during its solidification, and since eutectic cast iron solidi-

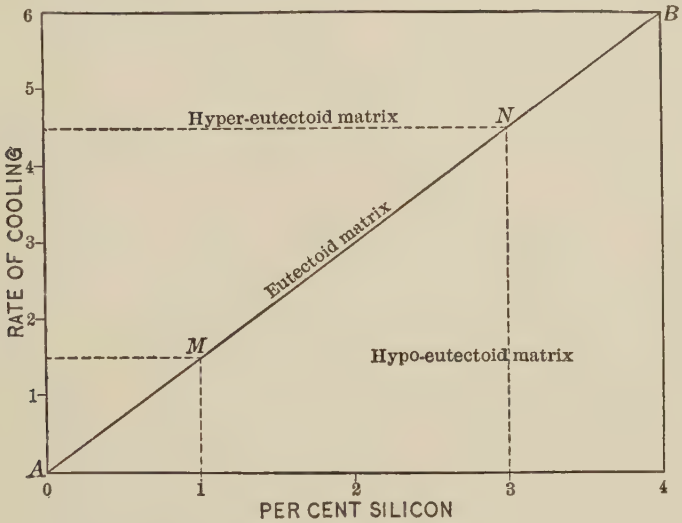


Fig. 335a. — Influence of silicon content and of rate of cooling in determining the character of the matrix of cast iron.

fies quickly while its temperature remains constant, whereas the solidification of hypo- and hyper-eutectic alloys cover wider ranges of falling temperature, it seems reasonable to infer, as already pointed out, that in eutectic cast iron the graphite must occur in smaller and more rounded particles. In other words the mushy, semi-fluid condition of relatively long duration assumed by non-eutectic alloys on solidifying must promote the formation of coarse graphite particles. If this view is correct it follows that for otherwise like composition and like treatment, cast iron of eutectic composition should be the strongest. In following that line of thought the influence exerted by some impurities on the eutectic carbon ratio should not be overlooked. With some 2 to 3 per cent silicon, for instance, some 3.50 to 3.75 per cent carbon should yield the eutectic alloy.

Silicon and Rate of Cooling vs. the Matrix of Cast Iron and the Formation of Graphite. — It is well known that the presence of silicon in cast iron promotes the formation of graphitic carbon while a rapid rate of cooling during solidification opposes it and causes it to occur in particles of smaller size.

The combined action of the rate of cooling and of the silicon content in determining the character of the matrix of cast iron may be advantageously shown graphi-

cally as in Figure 335a. The abscissæ correspond to percentages of silicon, the ordinates to rates of cooling represented by arbitrary numbers, 2 indicating quicker cooling than 1, 3 quicker cooling than 2, etc. Any point on the line AB corresponds to a set of conditions producing a eutectoid matrix, while any point above AB refers to rates of cooling and silicon contents resulting in hyper-eutectoid, and below AB, in hypo-eutectoid matrix. The point M, for instance, on AB corresponds to 1 per cent of Si and a rate of cooling represented by 1.5, while N corresponds to 3 per cent of Si and a quicker rate of cooling, 4.4. Both sets of conditions will produce castings having a eutectoid matrix *but not identical properties, because the quicker cooling in the latter case must produce smaller and less angular graphite particles and hence a stronger metal.*

Cast Iron of Maximum Strength. — From the foregoing considerations the following conclusions may be drawn: (1) to possess maximum strength, cast iron should be of eutectic composition because the graphite particles will then be smaller, which in turn makes for greater strength; (2) the eutectic structure should be produced by high silicon and low carbon content since the latter promotes strength; (3) the cast iron should have a eutectoid matrix because it is the matrix of greatest strength, and (4) the eutectoid matrix should be produced by high silicon content and rapid cooling because the latter leads to the formation of small graphite particles.

Solidification of Eutectic Cast Iron. — The mechanism of the solidification of eutectic cast iron and of its subsequent transformation on slow cooling may be illustrated graphically as shown in Figure 336, assuming that no graphite forms. $ABCD$ represents a block of eutectic cast iron cooling from above its melting point to atmospheric temperature. Above its liquidus-solidus line EF the metal is liquid. On reaching that line, which in pure iron-carbon alloys corresponds to a temperature of 1130 deg. C., it solidifies as an austenite-cementite eutectic containing EG (47.7 per cent) of austenite and GF (52.3 per cent) of cementite, as later explained. On cooling from the solidus to the eutectoid line HL or Ar_1 point, at about 700 deg. C., the eutectic austenite rejects cementite (pro-eutectoid cementite) until it reaches the eutectoid composition (0.85 per cent of C or 12.75 per cent of Fe_3C). The pro-eutectoid cementite thus formed joins the eutectic cementite and is represented by the triangle GIK in the diagram. Clearly IL represents the total free cementite in the alloy when it reaches its eutectoid point. On cooling through this point the remaining austenite, now of eutectoid composition, breaks up into ferrite and cementite to form pearlite, a constituent which contains about 12.75 per cent of cementite (OI in the diagram) and 87.25 per cent of ferrite (HO in the diagram). Finally, then, the completely cooled alloy contains ND per cent of cementite of eutectic origin, MN per cent of cementite of pro-eutectoid origin, PM per cent of eutectoid cementite, and CP per cent of ferrite. The eutectic and pro-eutectoid cementite known collectively as "free" or "excess" cementite (MD) are so merged that they cannot be distinguished from each other, while the eutectoid cementite exists as a distinct constituent of pearlite. In the diagram, PD represents the total cementite (free and eutectoid) in the alloy, and CP the ferrite, that is its ultimate structural composition.

Solidification of Hyper-Eutectic Cast Iron. — The mechanism of the solidification of hyper-eutectic cast iron and of its subsequent transformation on slow cooling may be represented graphically, as shown in Figure 337. It is assumed in this diagram that no graphitic carbon is formed.

On reaching its liquidus, EF, in the vicinity of 1,200 deg. C. in the case of a pure

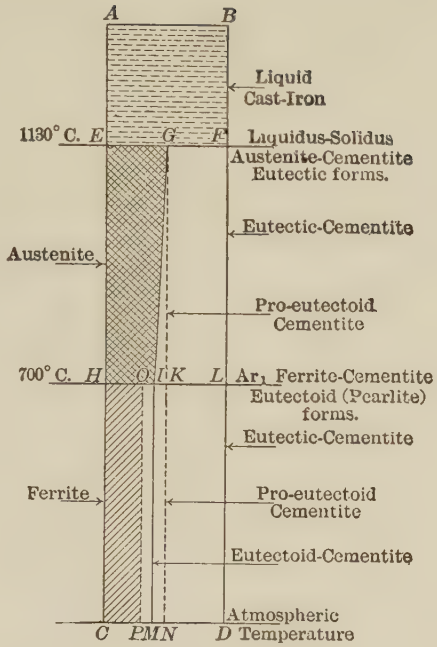


Fig. 336. — Diagram illustrating the mechanism of the solidification of eutectic cast iron.

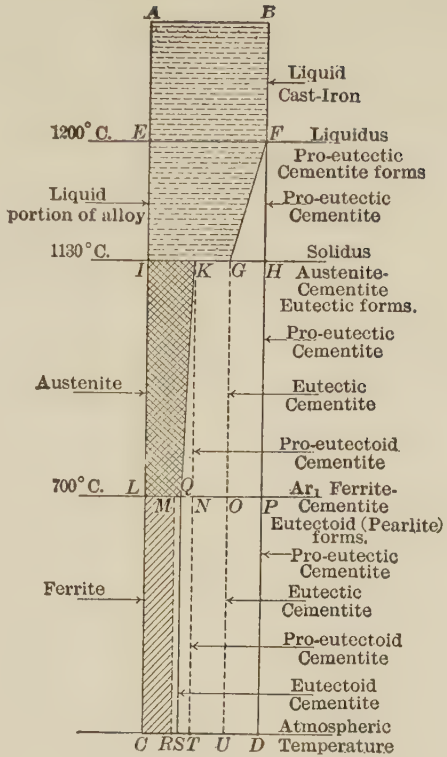


Fig. 337. — Diagram illustrating the mechanism of the solidification of hyper-eutectic cast iron.

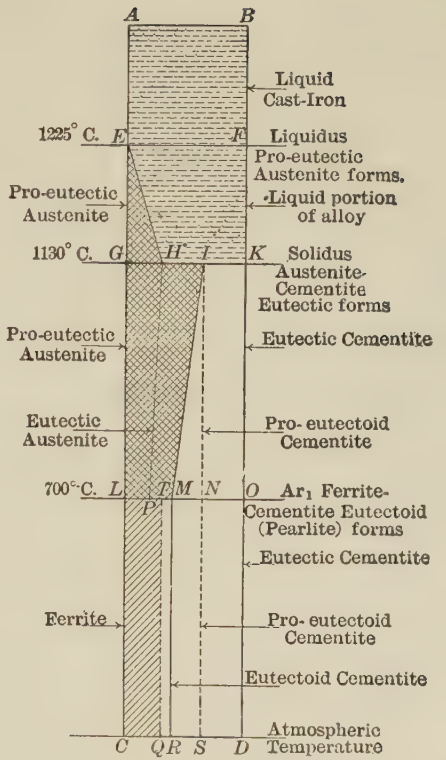


Fig. 338. — Diagram illustrating the mechanism of the solidification of hypo-eutectic cast iron.

alloy containing 5 per cent of carbon, cementite begins to form, and its formation continues to the solidus line, as indicated by the triangle *FGH*. On reaching the solidus (1130 deg. C.) the molten portion of the alloy has the eutectic composition (4.30 per cent of carbon), and it solidifies as an austenite-cementite eutectic, *IG*, containing *IK* per cent of austenite and *KG* per cent of cementite. This is in accordance with the solidification of the molten solution of any two metals capable of forming a eutectic alloy, as explained in Chapters XXIV and XXV. On cooling from its solidus to its eutectoid or Ar_1 point (700 deg. C.) the eutectic austenite rejects cementite, as indicated by the triangle *KQN*, until, on reaching the eutectoid point, it is of eutectoid composition, and is converted into pearlite containing *LM* per cent of ferrite and *MQ* per cent of cementite. The alloy will finally consist of *UD* per cent of pro-eutectic cementite, *TU* per cent of eutectic cementite, *ST* per cent of pro-eutectoid cementite, *RS* per cent of eutectoid cementite, and *CR* per cent of ferrite. The pro-eutectic, eutectic, and pro-eutectoid cementites are merged, and cannot be distinguished from each other under the microscope. Their sum, *SD*, constitutes the free cementite of the alloy. The eutectoid cementite, *RS*, on the contrary, remains intimately associated with the ferrite to form the constituent pearlite, represented by *CS* in the diagram. *RD* represents the total percentage of cementite in the alloy.

Solidification of Hypo-Eutectic Cast Iron. — The mechanism of the solidification of hypo-eutectic alloys may likewise be graphically represented as shown in Figure 338. On reaching its liquidus, *EF*, pro-eutectic austenite containing 1.70 per cent of carbon begins to form. Assuming the cast iron to contain 3.50 per cent of carbon, its temperature would then be in the vicinity of 1225 deg. C. In cooling from the liquidus to the solidus or eutectic temperature, *GK*, austenite continues to form, the percentage of that constituent solidifying between the liquidus and the solidus being represented by the triangle *EGH*. On reaching the eutectic temperature, the liquid portion of the alloy has reached the eutectic composition and now solidifies as an austenite-cementite eutectic, *HK*, containing *HI* per cent of austenite and *IK* per cent of cementite, following in this the behavior of all binary alloys in which a eutectic alloy is formed (Chapters XXIV and XXV). On cooling from the eutectic to the eutectoid or Ar_1 temperature, both the pro-eutectic and the eutectic austenite reject cementite, as indicated by the triangle *IMN*. At the eutectoid temperature, *LO*, the remaining austenite is of eutectoid composition and is transformed into pearlite, *LM*, containing *LT* per cent of ferrite and *TM* per cent of cementite. Below the eutectoid temperature, therefore, the cast iron consists of *CR* per cent of pearlite and *RD* per cent of free cementite, the pearlite containing *CQ* per cent of ferrite and *QR* per cent of cementite, and the free cementite *RS* per cent of cementite of eutectic origin, and *SD* per cent of cementite of pro-eutectoid origin. *QD* evidently represents the total cementite in the alloy.

The Graphitizing of Cementite. — It is well known, as more fully explained in Chapters XXIII and XXV, that cementite readily breaks up into iron (ferrite) and graphite when heated to a sufficiently high temperature, and it is likewise well known that the higher the temperature the more easily does this dissociation take place, and that silicon also promotes it. Bearing in mind the influence of temperature on the graphitization of cementite, we are justified in assuming that the higher the temperature at which cementite forms the more readily will it be converted into ferrite and graphite on subsequent cooling. It follows from the foregoing assumption that

the graphitization of the cementite formed in iron-carbon alloys during and below their solidification will take place in the following order with increasing difficulty: (1) graphitization of pro-eutectic cementite, (2) graphitization of eutectic cementite, (3) graphitization of pro-eutectoid cementite, and (4) graphitization of eutectoid cementite.

Graphitizing of Hyper-Eutectic Alloys. — In hyper-eutectic alloys pro-eutectic cementite forms as soon as the alloy begins to solidify and keeps on forming to the eutectic temperature. At such high temperature the dissociation tendency is so great that graphite very readily forms, even in the absence of silicon and during relatively rapid cooling. If time be given, the graphite resulting from the dissociation of pro-eutectic cementite rises to the surface of the still liquid bath, when it is known as "kish." Upon reaching the eutectic temperature, eutectic cementite forms, which easily breaks up into iron and graphite if the cooling be sufficiently slow, its graphitization being assisted by the presence of *nuclei* of pro-eutectic graphite. In cooling from the eutectic to the eutectoid temperature pro-eutectoid cementite is expelled by the austenite. The graphitization of pro-eutectoid cementite, however, proceeds with less readiness because of the relatively low temperature now prevailing, although assisted by the presence of many *nuclei* of pro-eutectic and eutectic graphite. A large percentage of silicon and very slow cooling would of course promote it. If some of the pro-eutectoid cementite fails to be graphitized the resulting cast iron will necessarily have a hyper-eutectoid matrix and will probably be mottled. Upon reaching the eutectoid temperature eutectoid cementite is formed, but its graphitization, although greatly assisted by the presence of much graphite, will require, at least to be complete, very slow cooling and the presence of considerable silicon. It is, of course, evident that if some pro-eutectoid cementite has escaped graphitization none of the eutectoid cementite will graphitize, since the dissociation of cementite becomes more difficult as the temperature is lowered. In case the graphitization of eutectoid cementite is complete, a rare instance, the resulting cast iron has a pure, or rather carbonless, ferrite matrix. If it is incomplete the matrix will be hypo-eutectoid and the cast iron belong to one of the foundry grades.

Graphitizing of Eutectic Alloys. — On reaching the solidification temperature eutectic cementite is formed, which breaks up quite readily into ferrite and graphite unless prevented from doing so through rapid cooling. On cooling from the eutectic to the eutectoid temperature pro-eutectoid cementite forms, the graphitization of which is promoted by the presence of *nuclei* of eutectic graphite but opposed by the lower temperature now prevailing. It may, however, be complete in the presence of sufficient silicon. If it remains incomplete the cast iron will have a hyper-eutectoid matrix. The graphitization of the eutectoid cementite formed at the eutectoid temperature is much less readily brought about, being now opposed by the low temperature of the metal. It will generally remain incomplete and the resulting cast iron will have a hypo-eutectoid matrix.

Graphitizing of Hypo-Eutectic Alloys. — In hypo-eutectic alloys when solidification begins austenite is formed, and at the eutectic temperature eutectic cementite falls out of solution. This cementite undergoes graphitization quite readily because of the high temperature at which it forms. On cooling from the eutectic to the eutectoid temperature pro-eutectoid cementite is rejected by austenite, and its graphitization proceeds the more slowly that it is not now assisted by preëxisting *nuclei* of graphite to the same extent as eutectic and hyper-eutectic alloys. The eutectoid

cementite is graphitized with difficulty because of low temperature and of relatively little preëxisting graphite. If the graphitization of pro-eutectoid cementite remains incomplete the cast iron will have a hyper-eutectoid matrix, while in case of complete graphitization of the pro-eutectoid cementite but incomplete graphitization of eutectoid cementite it will have a hypo-eutectoid matrix. In case of complete graphitization of the pro-eutectoid cementite and of no graphitization at all of the eutectoid cementite the cast iron would have a eutectoid matrix.

Seasoning of Cast-Iron Castings. — Castings of cast iron contain strains which gradually decrease with time — a phenomenon sometimes called seasoning. Tumbling through the action of slight blows frequently repeated relieves these internal strains, and therefore like seasoning increases the strength. Moldenke writes that a half-hour tumbling is equivalent to six months' seasoning, and that the increase of strength may amount to 35 to 40 per cent.

Growth of Cast Iron on Repeated Heating and Cooling. — It was shown many years ago by Outerbridge that after repeated heating and cooling gray cast iron grows enormously in cubical dimensions, growth exceeding 40 per cent having been observed. After forty heatings at 787 to 842 deg. C., each one of four hours' duration, the specific gravity of the iron had fallen from 7.25 to 5.49.

Heat Treatment of Cast Iron. — Since gray cast-iron castings may be considered as made up of a steel matrix in which numerous plates of graphite are embedded, it naturally follows that it should be possible through suitable heat treatments greatly to modify the physical properties of these castings. It should be possible at will to produce pearlitic, sorbitic, troostitic, or martensitic matrixes, hence to secure softness, strength, or hardness in accordance to requirements, and of course dependent also upon the chemical composition. The possibility of heat treatment applied to cast iron does not seem to have received adequate attention.

CHAPTER XXII

IMPURITIES IN CAST IRON

In the preceding chapter cast iron has been considered as a pure alloy of iron and carbon, but like steel, commercial cast iron always contains varying proportions of silicon, manganese, phosphorus, and sulphur, and we should now examine the influence of these impurities on its structure and consequently on its properties.

Silicon in Cast Iron. — Cast iron seldom contains less than 0.50 per cent silicon and frequently as much as 3 or 3.50 per cent. As in the case of steel this silicon probably combines with some of the iron to form the silicide of iron, FeSi, which is then dissolved in the balance of the iron. The ferrite of cast iron, therefore, always holds a considerable amount of silicon, or rather of the silicide FeSi, in solution. It has been seen that silicon produces exactly three times its own weight of FeSi; cast iron with 2 per cent of silicon, for instance, will contain 6 per cent of FeSi dissolved in its ferrite. The influence of silicon on the properties of cast iron is very important, chiefly through its promoting the formation of graphitic carbon, and therefore increasing the softness, and if carried too far, decreasing the strength of cast iron. It is why foundrymen often speak of silicon as a "softener." The influence of silicon in causing the decomposition of the carbide Fe_3C is ascribed by Stead, Hatfield, and others to the presence of some silicon in the carbide, which is thereby rendered less stable. That silicon increases fluidity while decreasing shrinkage and chill is also well known.

The influence of silicon to decrease the percentage of carbon in the iron-carbon eutectic has been considered in the preceding chapter.

The occurrence of varying amounts of silicon in cast iron cannot be detected under the microscope, unless indirectly and roughly through the presence of more or less graphitic carbon. It is probably true, however, that under otherwise similar conditions, the more silicon present in ferrite the slower the etching of that constituent. The ferrite of cast iron with hypo-eutectoid matrix, for instance, possibly because of its greater silicon content, often remains brilliant after the usual deep etching treatment which would color decidedly some of the grains of the ferrite of wrought iron or of low carbon steel.

Sulphur in Cast Iron. — Cast-iron castings of good quality should not contain more than 0.1 per cent of sulphur while but a trace of that element may be present. In the manufacture of chilled castings, however, as much as 0.2 per cent sulphur is sometimes allowed. It has been explained in Chapter VI that because of the great affinity of manganese for sulphur these two elements readily combine to form the manganese sulphide MnS, each part by weight of sulphur giving rise to the formation of approximately 2½ parts of MnS. Cast iron with 0.05 per cent sulphur, for instance, would contain about 0.125 per cent of MnS. As in the case of steel this sulphide occurs in the form of rounded particles of a dove gray or slate color embedded

in the metallic matrix (Fig. 339). Should there not be enough manganese present to combine with all the sulphur, the remaining sulphur would unite with iron to form the sulphide FeS which would occur as rounded yellow areas. It should be noted, however, that since it requires less than 2 parts by weight of manganese to combine with 1 part of sulphur, when cast iron contains twice as much manganese as it does sulphur no iron sulphide can be formed, theoretically at least. Since it is seldom that cast iron does not contain a considerably greater proportion of manganese the occurrence of FeS in cast iron should be rare.

The influence of sulphur in opposing the formation of graphitic carbon has already been mentioned; it may consequently be said to harden cast iron. Hatfield believes

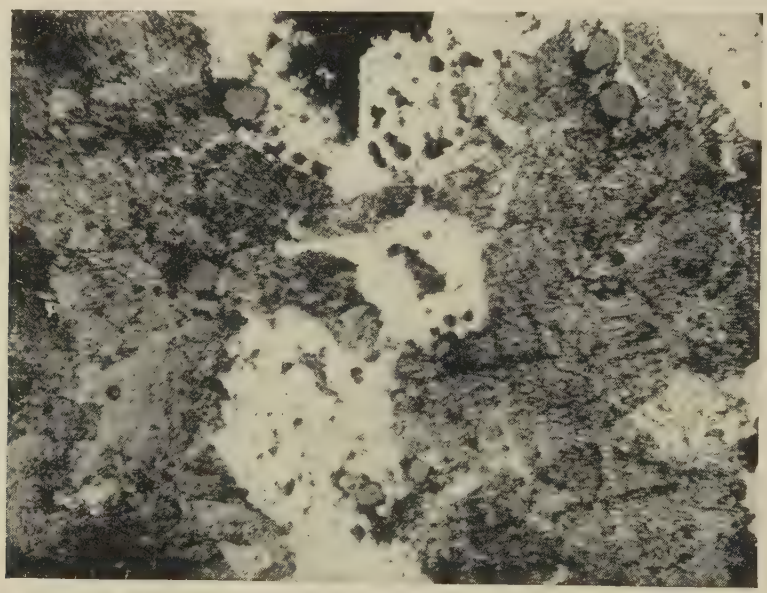


Fig. 339. — Partially malleablized cast iron. Magnified 670 diameters. Sulphur about 0.2 per cent, manganese 0.50 per cent. (C. C. Buck, Correspondent Course student.)

that this influence of sulphur is due to the presence of some sulphide of iron dissolved in the iron carbide and increasing its stability. It has also a well-known influence in increasing the depth of "chill" in solidifying cast iron against a metal wall, that is the thickness of metal free from graphitic carbon produced by the cooling action of that wall. Its other influences are harmful, as it increases shrinkage, causes the molten metal to be sluggish, and induces unsoundness.

Manganese in Cast Iron. — Special cast irons are made, known as spiegeleisen, ferro-manganese, etc., containing very large proportions of manganese, but in ordinary castings the amount of manganese seldom exceeds 2 per cent and may be as low as 0.10 per cent. It has been shown in Chapter VI that when manganese is present in these relatively small proportions it first combines with sulphur to form the sulphide MnS, and then with carbon to form the carbide Mn_3C, this carbide uniting with the carbide Fe_3C to form cementite. The cementite of cast iron, therefore, like that of steel, nearly always contains some Mn_3C. Since iron and manganese, however, have nearly the same atomic weight it remains true that to obtain the percentage of cement-

ite in any commercial iron-carbon alloy it suffices to multiply its percentage of combined carbon by fifteen.

The influence of manganese in opposing the formation of graphitic carbon has already been noted. It is explained by some on the ground that the carbide Mn_3C is more stable than Fe_3C. Like sulphur, manganese is a hardener, its presence in large

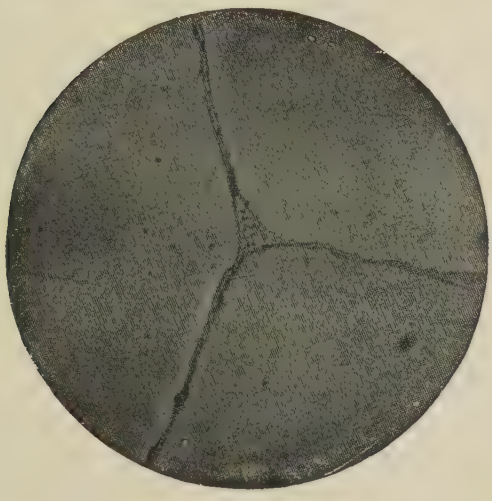


Fig. 340. — Alloy of iron and phosphorus. Phosphorus 1.8 per cent. Magnified 350 diameters. (Stead.)

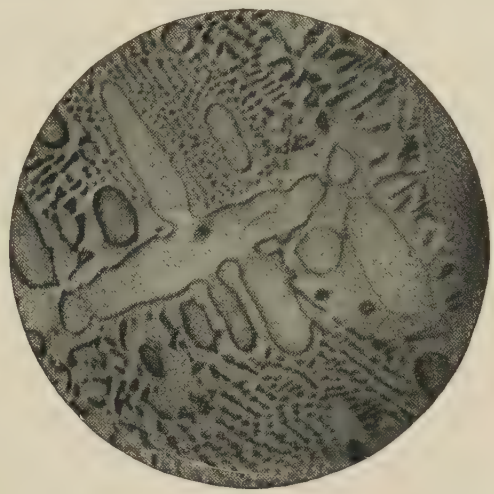


Fig. 341. — Alloy of iron and phosphorus. Phosphorus 8 per cent. Magnified 250 diameters. (Stead.)

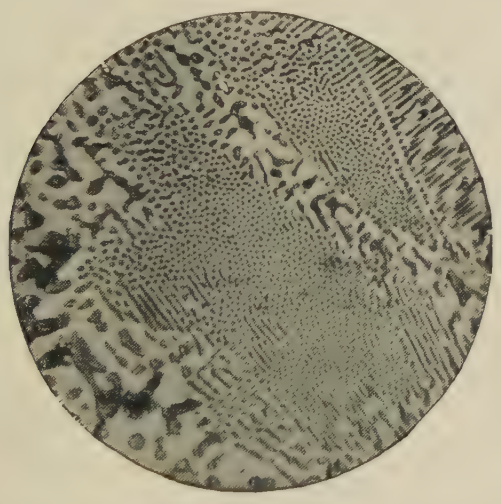


Fig. 342. — Alloy of iron and phosphorus. Phosphorus 10.2 per cent. Magnified 350 diameters. (Stead.)

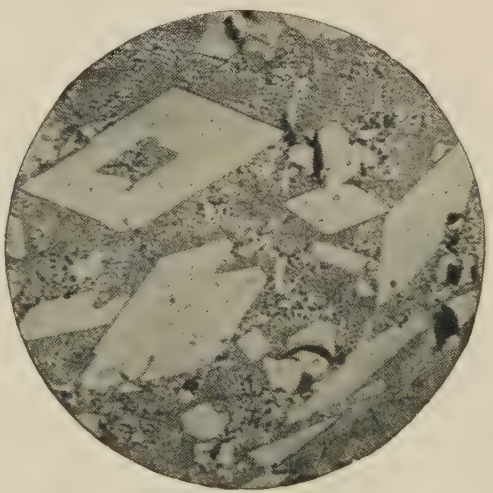


Fig. 343. — Alloy of iron and phosphorus. Phosphorus 11.07 per cent. Magnified 60 diameters. (Stead.)

proportions increasing the difficulty of machining castings. It promotes the absorption of carbon by iron. Some believe that it increases shrinkage and that while it has no marked influence on the depth of the chill it increases its hardness.

Phosphorus in Cast Iron. — It has been explained in Chapter VI that when phosphorus occurs in very small quantities, as it does in steel, the totality of it prob-

ably forms the phosphide Fe_3P, which is then dissolved by the iron. In cast iron, however, because of the frequent presence of a considerable proportion of phosphorus and of a larger proportion of carbon, this element assumes another condition. The occurrence of phosphorus in cast iron was first studied and described by Stead. The results of his important investigations are briefly summarized below:

(1) When phosphorus is alloyed with carbonless iron in amounts varying from traces to 1.70 per cent, it forms a phosphide corresponding to the formula Fe_3P, which is held in solid solution by the iron. All the metals used commercially, such as wrought iron and steels containing very little carbon, may be included in this class. They consist essentially of polyhedral grains of ferrite holding Fe_3P in solution.

(2) When the metal contains from 1.70 to 10.2 per cent phosphorus it consists of a saturated solution of Fe_3P in iron (1.70 per cent P) and of a eutectic alloy containing about 10.2 per cent P and made up of about 61 per cent Fe_3P and 39 per cent of the saturated solution of Fe_3P in iron. To account readily for this structure and that of the following groups, it is only necessary to consider these metals as alloys of two constituents: one the phosphide Fe_3P, and the other a saturated solution of Fe_3P in iron. It is well known that a certain class of binary alloys when solidifying give rise to the formation of a eutectic alloy, that is, of a mechanical mixture made up in definite proportions of extremely small plates alternately of one and the other constituents, the balance of the mass consisting of that constituent which is present in excess over the amount required to form the eutectic alloy. It is precisely what happens in the case of iron containing over 1.70 per cent phosphorus. The formation of eutectic alloys will be further described in Chapter XXIV.

Figures 340, 341, and 342 illustrate the structure of iron containing respectively 1.8, 8, and 10.2 per cent phosphorus. The mottled constituent made up of two structural elements in close juxtaposition corresponds in every case to the phosphide eutectic. The background of Figure 340 and the clear regions of Figure 341 are composed of the solid saturated solution, while Figure 342 is composed entirely of the eutectic alloy.

(3) When the iron contains from 10.2 per cent to 15.58 per cent phosphorus it is composed of crystals of Fe_3P surrounded by the eutectic mixture just described, as illustrated in Figure 343, in which the white angular areas represent Fe_3P and the background the eutectic alloy.

When carbon is present in considerable quantity as in cast iron, the phosphorus held in solution by the iron in the absence of carbon is thrown out of solution almost completely and a ternary eutectic formed (Stead, Wüst, Gœrens) containing, according to Stead, 91.19 per cent iron, 6.89 per cent phosphorus, and 1.92 per cent carbon, its proximate constituents being iron carbide (Fe_3C), iron phosphide (Fe_3P), and iron (ferrite) containing a little phosphorus in solution. After heat tinting, the constituents of the ternary eutectic are readily distinguishable, the iron carbide being colored red, the iron phosphide purple, and the ferrite containing some phosphorus in solution, white. While such is the character of the phosphide eutectic in white and mottled cast iron, Stead writes that in very gray phosphoretic metals the carbon diffuses out of it and a binary eutectic of Fe_3P and iron containing in solution a little phosphorus is formed. For this binary phosphide eutectic of gray cast iron first described by Stead in 1900 the author proposed the name of "steadite." It contains, according to Stead, about 10 per cent phosphorus and 90 per cent iron.

The structures of some iron alloys containing 1.70 per cent phosphorus and increasing proportions of carbon are illustrated in Figures 344 to 346. The increasing proportion of phosphorus thrown out of solution as a eutectic will be noted.

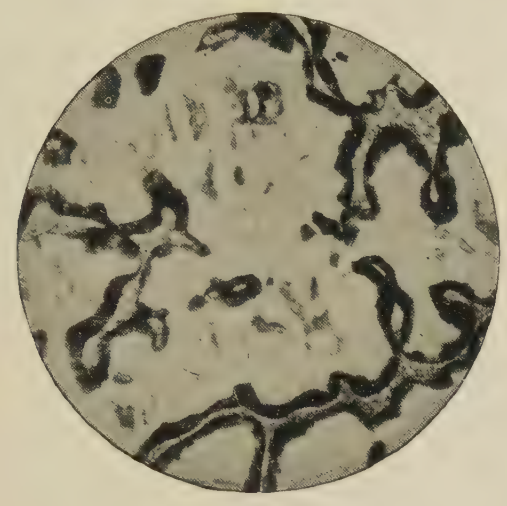


Fig. 344. — Alloy of iron, phosphorus, and carbon. Phosphorus 1.74 per cent, carbon 0.18 per cent. Magnified 60 diameters. (Stead.)

Fig. 345. — Alloy of iron, phosphorus, and carbon. Phosphorus 1.70 per cent, carbon 0.71 per cent. Magnified 250 diameters. (Stead.)

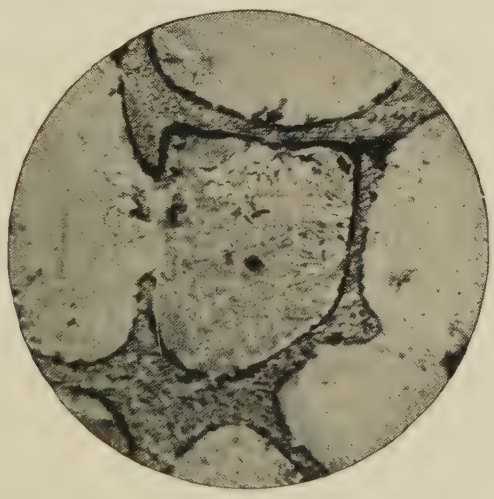


Fig. 346. — Alloy of iron, phosphorus, and carbon. Phosphorus 1.70 per cent, carbon 1.40 per cent. Magnified 250 diameters. (Stead.)

It will be obvious from the above description of the behavior of phosphorus that in cast iron, because of the presence of a large amount of carbon, nearly the whole of the phosphorus is liberated from its solution with iron and caused to occur as a ternary eutectic in white and mottled cast iron and as a binary eutectic or steadite in gray cast iron, even if the metal contains less than the necessary amount of phosphorus needed to saturate the iron, namely 1.70 per cent. Indeed so marked is this

Fig. 347. — Cast iron. Graphitic carbon 3.06 per cent. Combined carbon 0.08 per cent. Phosphorus 1.36 per cent. Magnified 100 diameters. (F. H. Franklin of Saunders and Franklin.)

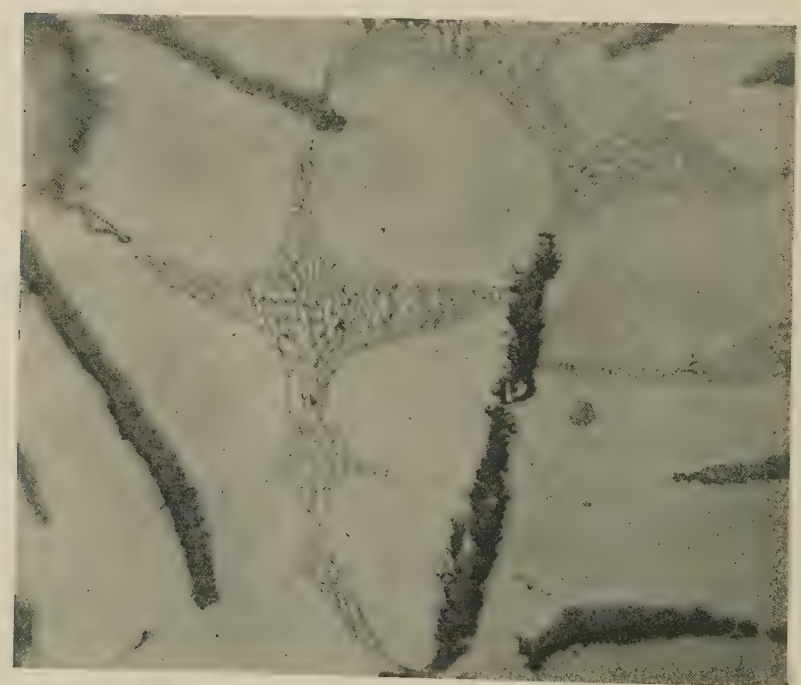


Fig. 348. — Same as Fig. 347 but magnified 425 diameters. (F. H. Franklin of Saunders and Franklin.)

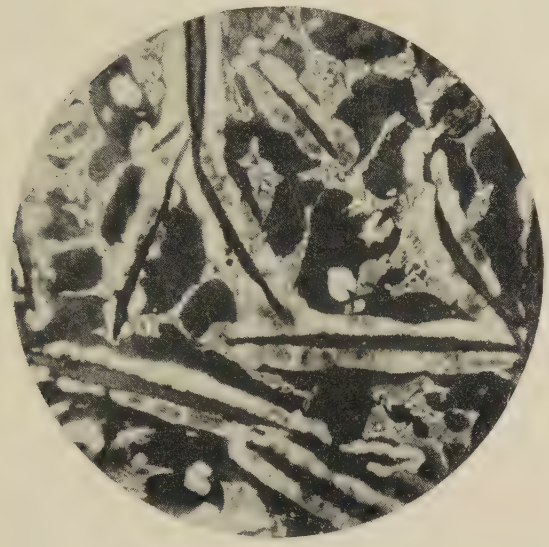


Fig. 349. — Cast iron. Magnified 100 diameters. Graphite, ferrite, pearlite, and steadite. (Boylston.)

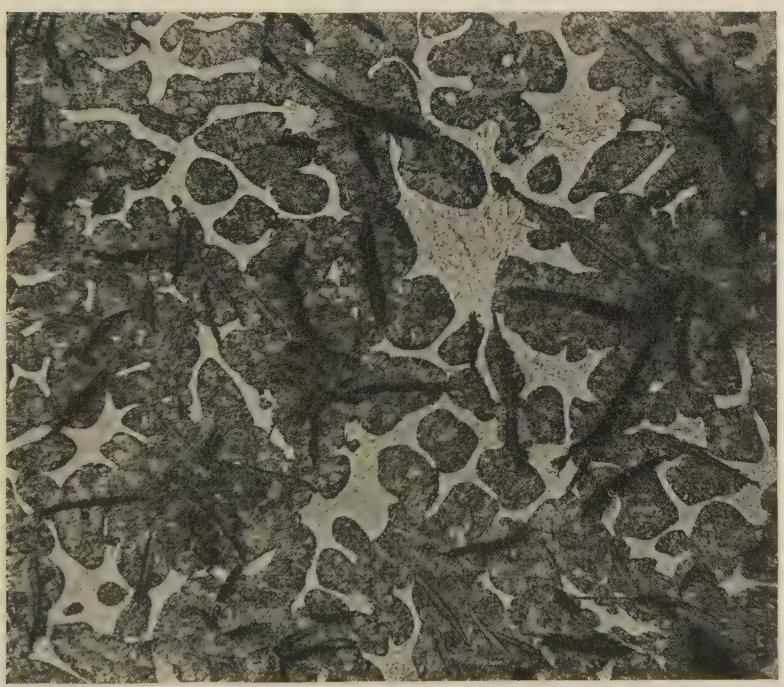


Fig. 350. — Cast iron. Eutectoid matrix. Phosphorus 1.36 per cent. Magnified 100 diameters. (F. H. Franklin of Saunders and Franklin.)

action of carbon that Stead tells us that in steel containing but 0.1 per cent phosphorus a portion of it is liable to be thrown out of solution in the presence of 0.90 per cent carbon.

To sum up, the phosphorus in ordinary steels occurs chiefly and probably alto-

gether as the phosphide Fe_3P dissolved in iron, while in cast iron it occurs chiefly if not entirely as a eutectic. While Stead writes that the whole of the phosphorus is not liberated from solution even in the presence of much carbon, the amount retained in solution in the presence of some 3 per cent or more carbon is apparently very small, and it may probably be assumed for all practical purposes that in cast iron the whole of the phosphorus is present as a eutectic, for Stead says that the phosphide eutectic may be detected in cast iron containing as little as 0.03 per cent phosphorus. The structure of gray phosphoretic cast iron is illustrated in Figures 347 to 350. The various constituents, graphite, pearlite, free ferrite, and steadite are easily distinguishable as follows: dark plates, graphite; dark, rounded constituent, pearlite; white, structureless, ferrite; white, mottled (dotted), steadite. The structure of the phosphide eutectic is shown more highly magnified in Figure 348. The matrix of the cast iron illustrated in Figures 347 and 348 is free from combined carbon, consisting, therefore, exclusively of ferrite and steadite; in Figure 349 the matrix contains both considerable pearlite and free ferrite; the cast iron shown in Figure 350 has a eutectoid matrix.

Stead recommends heat tinting as a suitable treatment for bringing out the phosphide eutectic, especially in white cast iron when there is danger of confounding it with cementite.

Stead explains as follows the fact that a relatively high proportion of phosphorus in cast iron does not produce extreme brittleness.

"The reason why phosphoretic pig irons are not more brittle than they are is because the eutectic separates into isolated segregations and does not form continuous cells round the crystalline grains. When the phosphorus does not exceed 1.7 per cent the metal is comparatively strong, but an addition of 0.3 per cent reduces the strength materially, the reason of which is that the eutectic brittle areas in metal with 2 per cent phosphorus approach each other closely, leaving less of the strong ground mass intervening."

Phosphorus has no marked influence upon the condition in which carbon occurs in cast iron but it increases the fluidity of the metal probably because of the formation of a large quantity of this fusible and fluid phosphide eutectic.

An attempt has been made in Figure 351 to represent diagrammatically the behavior of phosphorus. Assuming, for instance, the presence of 1 per cent phosphorus (1) in steel, (2) in white cast iron, and (3) in gray cast iron, the diagram indicates that the corresponding structures will be: (1) 100 per cent pearlite, or pearlite and ferrite, or pearlite and cementite, the pearlite-ferrite and the free ferrite, if any, holding the phosphorus in solution; (2) AB per cent of pearlite and cementite, and BC per cent of a ternary eutectic, the composition of which is shown, and (3) AB per cent of graphite, BC per cent of pearlite, pearlite and ferrite, or pearlite and cementite, and CD per cent of a binary eutectic (steadite) made up of iron holding a little phosphorus in solution, and of Fe_3P.

Critical Points of Cast Iron Containing Phosphorus. — H. I. Coe has published the interesting and significant cooling curves of cast iron containing increasing proportions of phosphorus reproduced in Figure 352. In the six samples of cast iron involved the percentages of phosphorus were respectively 0.09, 0.53, 1.01, 1.23, 2.16, and 2.90. The two upper points correspond to the solidification of the iron-carbon alloys, as explained in Chapters XXIV and XXV, the third point to the solidification of the phosphide eutectic [1] and the fourth to the recalescence point (pearlite

[1] Stead indicates 980 to 1000 deg C. as the solidification point of the phosphide eutectic.

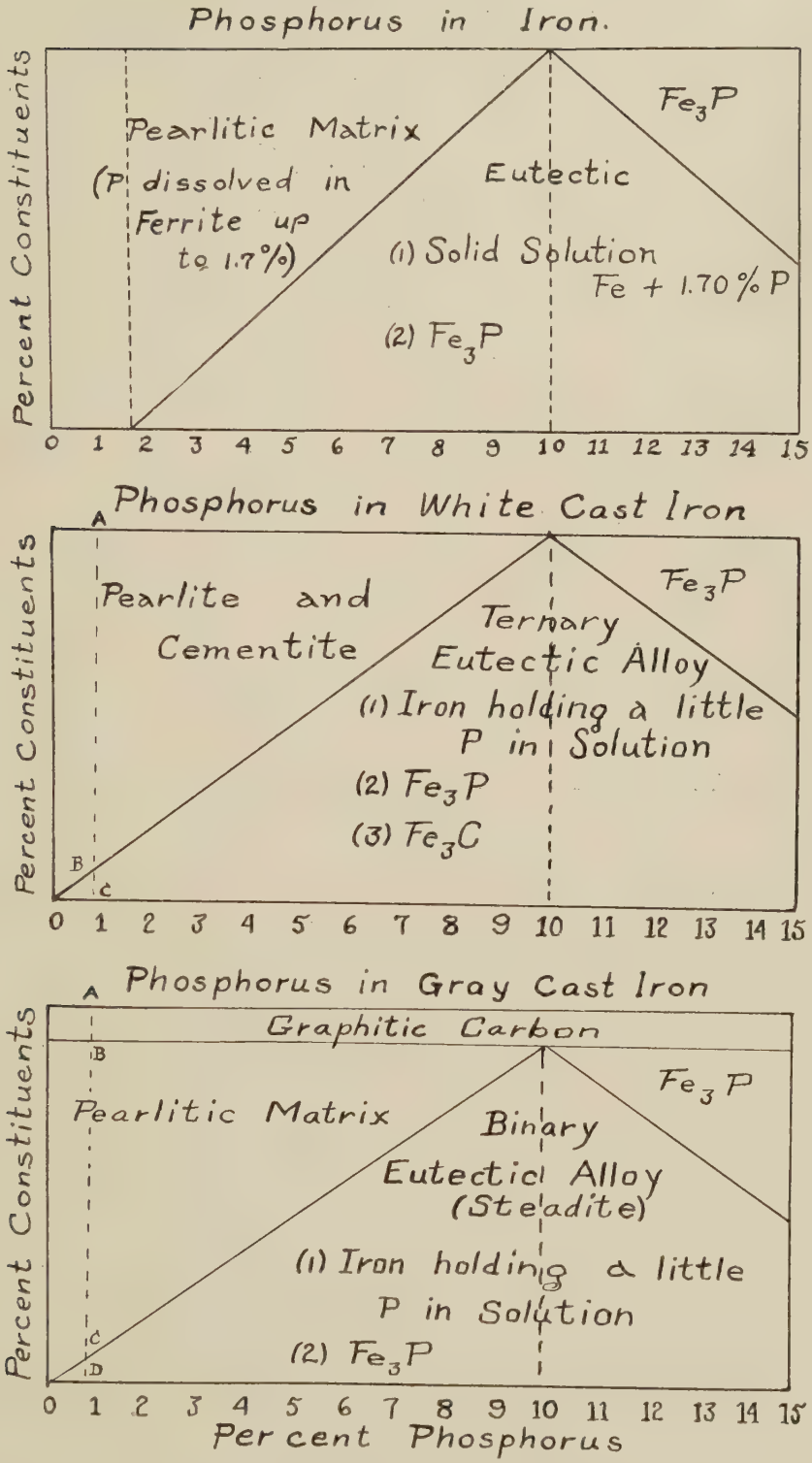

Phosphorus in Iron.
Percent Constituents
Pearlitic Matrix
(P dissolved in Ferrite up to 1.7%)
Eutectic
(1) Solid Solution Fe + 1.70% P
(2) Fe3P
Fe3P
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Phosphorus in White Cast Iron
A
Pearlite and Cementite
Ternary Eutectic Alloy
(1) Iron holding a little P in Solution
(2) Fe3P
(3) Fe3C
Fe3P
B
C
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Phosphorus in Gray Cast Iron
A
Graphitic Carbon
B
Pearlitic Matrix
Binary Eutectic Alloy (Steadite)
(1) Iron holding a little P in Solution
(2) Fe3P
Fe3P
C
D
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Per cent Phosphorus

Fig. 351. — Alloys of iron, carbon, and phosphorus.

formation). It is to be inferred from these curves that as phosphorus increases (*a*) the melting point of the alloy is lowered, (*b*) the intensity of the third point increases, (*c*) the position of the third point is slightly raised, and (*d*) the position of the point of recalescence remains practically unaffected.

Structural Composition of Phosphoretic Cast Iron. — Since the presence of 10.2 per cent phosphorus causes the production of 100 per cent steadite it follows that the phosphorus in cast iron gives rise to the formation of approximately 10 times its own weight of steadite.

In calculating the structural composition of cast iron, therefore, the amount of phosphorus present must be considered, as it may very materially lower the percent-

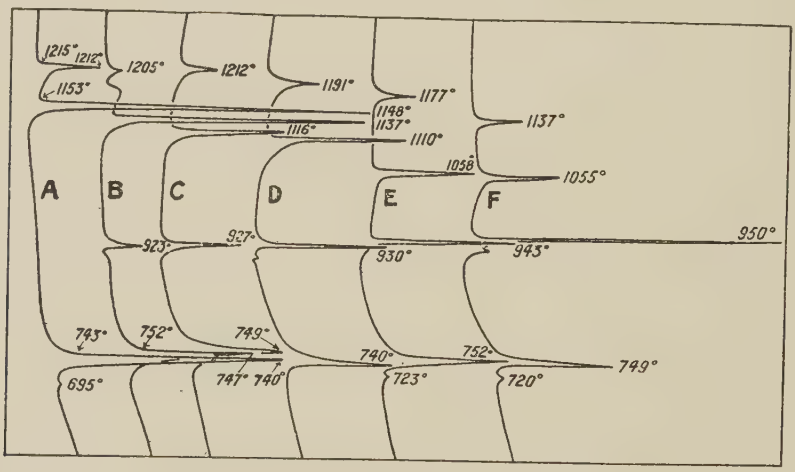


Fig. 352. — Cooling curves of cast-iron samples containing increasing percentages of phosphorus. (H. I. Coe.)

age of combined carbon needed to convert its matrix into pearlite. Bearing in mind that cast iron to be free from both free ferrite and free cementite must contain ferrite and cementite in the proportion of 6.8 to one the following relation will indicate the needed amount of combined carbon:

$$\text{Ferrite} = 100 - \text{G} - 10\,\text{Ph} - 15\,\text{C} = 6.8 \times 15\,\text{C} = 102\,\text{C}$$

(cementite)

or

$$100 - \text{G} - 10\,\text{Ph} - 117\,\text{C} = 0$$

in which G, C, and Ph represent respectively the percentage of graphite, combined carbon, and phosphorus, 15 C representing, of course, the proportion of cementite and 10 Ph that of steadite.

If the first term of the above equation is greater than 0 the metal will contain free ferrite, i.e. its matrix will be hypo-eutectoid; if it is smaller than 0 it will contain free cementite, i.e. its matrix will be hyper-eutectoid.

In the presence of 3 per cent of graphite and 1 per cent phosphorus, for instance, the percentage of combined carbon needed to produce a eutectoid matrix will readily be obtained in solving the equation

$$100 - 3 - 10 - 117\,\text{C} = 0$$

which calls for 0.74 per cent combined carbon. Less combined carbon would produce free ferrite, while more would cause the formation of free cementite.

In calculating the structural composition of any phosphoretic cast iron of known percentage of phosphorus, graphite, and combined carbon, it should first be ascertained, therefore, whether its matrix will be hypo- or hyper-eutectoid. Let us assume, for instance, a cast iron containing 1.50 per cent phosphorus, 3.25 per cent graphite, and 0.40 per cent combined carbon. Since $100 - 3.25 - 15 - 117 \times 0.40$ is greater than 0 the matrix of the iron will be hypo-eutectoid, that is the metal will contain free ferrite. The following equations will then permit the ready calculation of its structural composition.

$$(1)\ P + F + S + G = 100$$
$$(2)\ P = 117\ C$$
$$(3)\ S = 10\ Ph$$

which give

Pearlite (P)	= 46.80	per cent
Free ferrite (F)	= 34.95	" "
Steadite (S)	= 15.00	" "
Graphite (G)	= 3.25	" "
	100.00	" "

Taking another example, a cast iron containing 2 per cent graphite, 1.50 per cent combined carbon, and 0.75 per cent of phosphorus, since $100 - 2 - 7.50 - 117 \times 1.50$ is less than 0, the iron will contain free cementite. Its structural composition will be obtained by solving the equations

$$(1)\ P + Cm + S + G = 100$$
$$(2)\ P = \frac{7.8}{6.8}(100 - 15\ C - 10\ Ph - G) = 1.15\ (100 - 15\ C - 10\ Ph - G)$$
$$(3)\ S = 10\ Ph$$

which give

Pearlite (P)	= 78.22	per cent
Free cementite (Cm)	= 12.28	" "
Steadite (S)	= 7.50	" "
Graphite (G)	= 2.00	" "
	100.00	" "

Chemical vs. Structural Composition. — It will now be instructive to compare the chemical composition of cast iron both ultimate and proximate with its structural composition. To that effect let us assume a cast iron of the following ultimate chemical composition:

Graphitic carbon	3.00	per cent
Combined carbon	0.50	" "
Silicon	2.00	" "
Phosphorus	1.50	" "
Manganese	0.40	" "
Sulphur	0.02	" "
Iron (by difference)	92.58	" "
	100.00	" "

In view of the foregoing considerations the following proximate compounds will be formed:

(1) 0.02 per cent S will produce about 0.05 per cent MnS.
(2) 0.05 per cent MnS contains about 0.03 per cent Mn.
(3) This leaves 0.40 − 0.03 = 0.37 per cent Mn in excess to combine with carbon.
(4) 0.37 per cent Mn will form 0.39 per cent Mn_3C.
(5) 0.39 per cent Mn_3C contains about 0.02 per cent carbon.
(6) This leaves 0.50 − 0.02 = 0.48 per cent carbon to combine with iron.
(7) 0.48 per cent carbon will form 7.20 per cent Fe_3C.
(8) 1.50 per cent phosphorus will form 9.63 per cent Fe_3P.
(9) 2.00 per cent silicon will form 6.00 per cent FeSi.

The proximate chemical analysis of the cast iron considered will consequently be:

Graphitic carbon	3.00 per cent
Fe_3C	7.20 " "
Mn_3C	0.39 " "
Fe_3P	9.63 " "
FeSi	6.00 " "
MnS	0.05 " "
Iron (by difference)	73.73 " "
	100.00 " "

Knowing the proximate chemical constituents, the structural composition can be readily calculated. The Fe_3C and Mn_3C form the cementite, hence the cast iron contains 7.20 + 0.39 = 7.59 per cent cementite. The whole of this cementite, since the iron evidently has a hypo-eutectoid matrix, will combine with ferrite in the proportion of 6.8 to 1 to form pearlite, hence the cast iron will contain 7.59 × 7.8 = 59.20 per cent pearlite; 1.50 per cent phosphorus means 15.00 per cent of steadite; the 6.00 per cent of FeSi will be dissolved in the ferrite, while the small quantity of MnS will occur as independent minute particles. The structural composition will therefore be:

Pearlite (P)	= 59.20 per cent
Free ferrite (F) (by difference)	= 22.75 " "
Steadite (S)	= 15.00 " "
Graphite (G)	= 3.00 " "
MnS	= 0.05 " "
	100.00 " "

The quicker method for the calculation of the structural composition of cast iron given in foregoing pages, and in which the presence of manganese, silicon, and sulphur is ignored, would have given:

Pearlite (P)	58.50 per cent
Free ferrite (F)	23.50 " "
Steadite (S)	15.00 " "
Graphite (G)	3.00 " "
	100.00 " "

For practical purposes these values are identical to those obtained from a knowledge of the complete analysis of the iron.

Oxygen in Cast Iron. — J. E. Johnson has contended that oxygen strengthens and otherwise improves cast iron, while Moldenke blames oxygen for many of the ailments from which it occasionally suffers. Many doubt the presence of any appreciable amount of oxygen in cast iron.

Special Cast Irons. — The addition of some 14 per cent of silicon to cast iron imparts to it a very marked resistance to the action of acids. Some of these irons are known by their trade names — "Duriron" and "Tantiron." The addition of some 20 to 30 per cent chromium makes cast iron very resistant to oxidation at high temperatures. The commercial product known as "Thermalloy" belongs to this class.

Dendritic Structure of Cast Iron. — We may follow in our imagination the solidification of cast iron, (1) hypo-eutectic, and (2) hyper-eutectic, in an attempt at visualizing the probable formation of dendrites.

When hypo-eutectic cast iron reaches its solidification point, the solid solution (saturated austenite) which forms first should constitute the axes of the dendrites while the fillings of later solidification should contain the austenite-cementite eutectic. The phosphide eutectic, because of its lower melting point, should also be located in the fillings. In the presence of much phosphorus there should be a tendency on the part of the carbon to leave the fillings and to segregate in the axes in accordance with the action of phosphorus in expelling carbon, already discussed in these pages. On further cooling, including passage through the critical range, the austenitic axes are converted into pearlite and cementite as well as the austenite present in the eutectic.

In the case of hyper-eutectic cast iron, cementite, being the first constituent to solidify, should be located in the axes, while the cementite-austenite eutectic and the phosphide eutectic should occupy the fillings.

The granulations of the dendrites on further cooling, described in previous chapters, is here complicated by the graphitizing of cementite.

The dendritic crystallization of cast iron has not received the attention which it deserves.

CHAPTER XXIII

MALLEABLE CAST IRON

Graphitizing of Cementite. — The unstability of cementite has already been alluded to. It has been mentioned that the prolonged annealing of very high carbon steel above its critical range was always likely to result in the formation of some graphitic carbon through the dissociation of the unstable cementite according to the reaction:[1]

$$Fe_3C = 3\ Fe + C$$

It should be recalled here that some believe that above the critical range, carbon is not present as Fe_3C dissolved in gamma iron but that it occurs in atomic dispersion. They go so far as to indicate the precise position occupied by the carbon atoms in the crystal structure of gamma iron. The formation of graphite under these conditions must result in the atoms leaving in some way their assigned positions in the lattice structure and collecting into large particles readily visible under low power magnification. No attempt has been made to explain this mechanism. It will be assumed in these pages that above the critical range carbon is present as Fe_3C dissolved in gamma iron.

The graphitic carbon formed in this way is often called, according to Ledebur, "temper" carbon to distinguish it from the graphite formed during the solidification of cast iron. This breaking up of cementite into ferrite and graphite takes place the more readily (1) the more combined carbon in the metal, (2) the higher the temperature, (3) the longer the exposure to a high temperature, (4) the more silicon and the less manganese and sulphur present. The influence of a large amount of combined carbon in promoting the graphitizing of cementite is made evident by the facts (1) that iron-carbon alloys containing less than some 0.50 per cent carbon cannot be made graphitic under the most favorable annealing conditions even when containing

[1] According to Honda and Murakami the formation of graphite does not result from a direct decomposition of cementite but is due to a catalytic action of gases such as carbon monoxide or dioxide. They write:

"The mechanism of the catalytic action is assumed as follows: —

"As the temperature falls from the melting point, a minute quantity of carbon dioxide coexisting with carbon monoxide soon reacts on cementite, and produces carbon monoxide by equation

$$Fe_3C + CO_2 = 2\ CO + 3\ Fe;$$

this diminution or disappearance of carbon dioxide causes a further dissociation of carbon monoxide by equation,

$$2\ CO = CO_2 + C,$$

reproducing the dioxide, which reacts with cementite. Thus, these two reactions, being continuously repeated in the alloys, graphite is gradually produced with the consumption of cementite.

"The most favorable temperature for the graphitization is below the eutectic point, but above 1100 deg., and as the temperature decreases, graphitization becomes always less."

much silicon, (2) that in steel containing in the vicinity of 1 per cent carbon the graphitizing proceeds very slowly and remains partial, and (3) that in alloys containing 2.50 per cent or more of combined carbon and a sufficient amount of silicon the conversion of cementite into iron and graphite takes place readily and can be carried to completion, combined carbon disappearing altogether. The influence of temperature and time upon the dissociation of cementite was to be expected. Evidences will be presented in Chapter XXV to show that the higher the temperature at which cementite forms the more readily is it converted into iron and graphitic carbon, during solidification and subsequent cooling. The influence of silicon in graphitizing cementite could likewise have been anticipated because of its well-known power to cause the formation of graphitic carbon during and below solidification. It will be argued in Chapter XXV that the formation of graphite during solidification always results from the dissociation of cementite, that is, that cementite (Fe_3C) always forms first but being very unstable readily breaks up into iron and graphite, its dissociation being promoted (1) by slow cooling and (2) by the presence of silicon.

The conversion of combined carbon into graphitic or rather temper carbon finds an important industrial application in the manufacture of so-called malleable cast-iron castings, also termed "malleable castings," "malleable cast iron," and even "malleable" (pronounced "mallable").

The metallography of these castings should now be considered.

Malleable Cast-Iron Castings. — The adjective "malleable" always used in describing these castings is misleading, for it suggests a malleability and other properties akin to those of steels, which malleable castings are far from possessing. By malleability the metallurgist always understands that property which makes it possible to convert a metallic mass into commercial shapes by rolling, hammering, etc., and such degree of malleability is not present in malleable cast iron. The manufacture of malleable cast-iron castings consists in subjecting to a long annealing treatment cast-iron castings of suitable composition whereby some of the carbon may be expelled by oxidation while most if not the whole of that remaining is converted into graphite (temper carbon). The various factors influencing this operation will be briefly described.

Original Castings. — The castings to be subjected to the malleablizing treatment are often called "hard" castings because they are invariably made of white cast iron and are therefore very hard and brittle. The reason why the original castings must be made of white cast iron will be obvious if it be considered that the malleability to be imparted to these castings is to result chiefly, and in some cases altogether, from a conversion of combined carbon into temper carbon, as explained above. Any graphite particle existing in the casting will be unaffected by the annealing treatment and will be a source of weakness in the finished casting. Clearly, therefore, the hard castings should be free from graphitic carbon. As to the amount of carbon that should be present, theoretical considerations lead us to conclude that the less carbon the more ductile should be the castings after thorough malleablizing, for, after all, the particles of temper carbon while much less injurious than the hard, brittle cementite from which they are derived are nevertheless a source of weakness chiefly because of their breaking up the continuity of the metallic mass. Again a smaller proportion of carbon necessarily means a shorter annealing operation. The desirability of low carbon content in cast-iron castings to be malleablized is universally recognized and it is partly why a large proportion of these castings are made in the "air" furnace or open-

hearth furnace, as by their use the percentage of carbon can be lowered. On the other hand, as already mentioned, if the proportion of combined carbon be small the graphitizing takes place with greater difficulty. These considerations point to the existence of a lower as well as of an upper limit for the carbon content of hard castings. In the majority of cases the percentage of carbon varies between 2.50 and 3.00 per cent. According to Moldenke it should not be lower than 2.75 per cent.

The beneficial action of silicon has been referred to; it greatly promotes the graphitizing of the cementite. It might seem then as if the more silicon in the hard casting the better, at least up to some 2 or 3 per cent. Castings of white cast iron cannot be

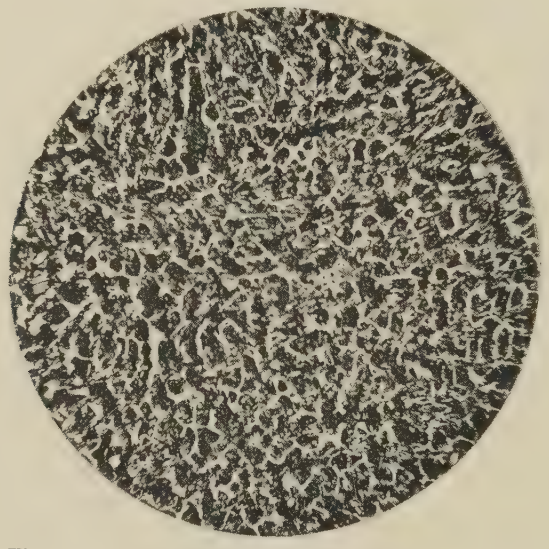


Fig. 353. — Hard casting (white cast iron). Magnified 67 diameters. (Boylston.)

made, however, in the presence of much silicon, since this element would cause the formation of graphitic carbon on solidification, even during quick cooling, and the casting would not be white. And since large castings will solidify more slowly than smaller ones it is evident that in large castings especially but a relatively small amount of silicon can be allowed. It is probably true that as much silicon should be introduced in the cast iron as will permit the making of white castings, and this proportion of silicon will necessarily decrease as the size of the casting increases. In practice it is found to vary between 0.30 per cent in large castings (4 inches thick or more) and 1.25 per cent in very small castings for like solidification conditions and subsequent cooling. In the majority of cases the silicon content varies between 0.50 and 1 per cent.[1] Moldenke writes that the best all-around percentage of silicon for general castings is 0.65. A. Lissner recommends 0.9 per cent silicon for castings one inch thick. Malleable castings are seldom more than ¾ inch thick.

In Moldenke's opinion the manganese should not exceed 0.60 per cent, as a larger amount is liable to cause trouble on annealing and difficulty in machining. Phos-

[1] According to A. Lissner doubling the sulphur reduces the speed of dissociation of the cementite 5 times, while an increase of 0.8 per cent silicon doubles the speed. The restraining effect of 0.05 per cent sulphur is neutralized by an increase of 0.28 per cent silicon.

phorus, according to the same authority, should not exceed 0.225 per cent, while sulphur should not exceed 0.07 and preferably not 0.05 per cent. These figures represent American practice only, for in Europe cast-iron castings being malleablized contain considerably more sulphur and phosphorus.

The structure of a hard casting of suitable composition for the malleablizing process is shown in Figure 353. It will be seen to be characteristic of the structure of white cast iron.

Annealing Operation. — The hard castings are placed in an annealing box and firmly packed in a suitable material. The boxes are then placed in the annealing furnaces and with their contents exposed to a desirable temperature for a suitable length of time. These various steps should be briefly considered.

Packing Materials. — The packing material affords a support for the castings while it may or may not play an important part in the process itself, according to its being (1) oxidizing or (2) non-oxidizing. In his pioneer work, in 1722, Réaumur surrounded white cast iron with crushed iron oxide, the oxygen of which removed a large proportion of the carbon during the subsequent long annealing treatment at a high temperature. Given a sufficiently high temperature and sufficiently long exposure, nearly the whole of the carbon could in this way be eliminated from small castings, a small amount of it only remaining as temper carbon. It will be evident that in the operation conducted in this way the oxidizing action of the packing is of more importance in producing malleability than the graphitizing of the cementite. The elimination of the carbon takes place through the well-known reaction between the iron oxide (from the packing) and the carbon in the steel,

$$3\ Fe_3C + Fe_2O_3 = 11\ Fe + 3\ CO$$

the cementite in the center migrating towards the outside and being in turn acted upon by the oxygen of the packing material.

It will be evident that this elimination must necessarily proceed from the outside to the center, so that if one should interrupt the operation after a relatively short time he would find an increasing proportion of carbon from shell to center. The use of an oxidizing and therefore chemically active packing material was for a long time considered essential in the malleablizing process. Later investigations, however, showed that white cast iron could be made malleable solely through the conversion of combined into graphitic carbon with very little if any removal of the carbon and that an oxidizing packing was not therefore necessary. Inert packing, such as sand and clay, may be used and satisfactory malleable castings produced. It is customary, however, in American practice, to use oxidizing packings but to depend chiefly on the graphitizing of cementite brought about by annealing for the desired malleability and strength. Although realizing that an oxidizing substance as a packing material is not indispensable, it is still preferred because of the apparent greater strength its use confers to the castings. The substances most used are powdered iron oxides in the shape of iron ore, mill scale, puddle cinder, "bull-dog," etc., and, according to Moldenke, the crushed flakes detached from the annealing pots themselves.

Annealing for Malleablizing. — The malleability imparted to white cast iron by annealing results from, as explained in the foregoing pages, (1) the hard, brittle cementite being converted into minute rounded particles of soft graphitic (temper) carbon and (2) the burning of some carbon by the oxygen of the packing materials. If we depend chiefly upon the burning of the carbon for the desired malleability, so-called

"white heart" castings are produced, while if the graphitizing of cementite is mainly sought, so-called "black heart" castings are obtained. The temperature and length of the annealing operation vary according to the kind of castings wanted.

The annealing operation is always conducted above the critical point $Ac_{3\cdot2\cdot1}$ of the white cast iron and of course below its solidification, that is when the metal exists as an aggregate of cementite and solid solution (saturated austenite), as explained in Chapter XXV.

When iron-carbon alloys contain less than 1.70 per cent carbon they consist exclusively, above their critical range, of the solid solution austenite.

When they contain more than 1.70 per cent carbon they are made up of an aggregate of cementite and of saturated austenite. Bearing in mind the difficulty of causing the graphitizing of cementite when the alloy contains less than 1.70 per cent carbon, that is when it is entirely austenitic, and the readiness with which it graphitizes when it contains more carbon, that is when it is an aggregate of cementite and saturated austenite, it seems plausible to infer that ease in graphitizing requires the presence of free cementite. It also seems probable that the free cementite graphitizes first and that the resulting particles of temper carbon act as nuclei for the graphitizing of the austenite cementite.

Annealing for "White Heart" Castings. — In the making of white heart castings a very large proportion of the carbon is removed by oxidation through the use (1) of an oxidizing packing, (2) of a high annealing temperature, and (3) of a long annealing. The original malleable castings made by Réaumur were of this type and his method is still much used in Europe. The castings are annealed for four or five days at a temperature of 800 to 900 deg. C. By removing some castings from the annealing box from time to time and examining their structure the progress of the operation may be readily observed. The following transformations are noted as the operation progresses: (1) a narrow white rim of decarburized metal caused by the burning of the carbon from the outside of the casting and a dark center caused by the graphitizing of some of the cementite; (2) a broader white rim and a smaller and darker core due to the burning of more carbon and to the formation in the center of the casting of more graphitic carbon, the graphitizing of the cementite being now indeed possibly complete; (3) the fracture of the metal is now white and steely to the very center, showing that most of the carbon has been removed by oxidation. These conclusions are fully confirmed by the microscopical examination of the structure of castings subjected to this annealing treatment for various lengths of time. As this oxidation of the carbon is necessarily a very slow process, white heart castings of small size only are made, generally not over ½ inch thick. For malleablizing larger castings the "black heart" process is decidedly superior.

White heart castings have a rather coarse fracture and structure because of the high and prolonged heating to which they were exposed. Since they resemble low carbon steels in composition and structure it would seem as if their properties could be very materially improved by suitable heat treatment, as, for instance, by annealing followed by cooling in oil or in air according to their carbon content. Moldenke states that the European white heart malleable castings bend excellently and are very good, though slightly weaker than black heart castings.

Annealing for "Black Heart" Castings. — For the production of black heart castings, since the oxidation of carbon is of secondary importance, the annealing temperature need not be so high, nor indeed is it necessary to use an oxidizing packing.

As already mentioned, oxidizing packings are generally used, however, because of the apparent greater strength they impart to the castings. A certain amount of carbon, therefore, is burnt at the surface of the casting, causing a narrow white rim, while the core is very dark, hence the name of black heart given to these castings. This dark-

Fig. 354. — Black heart malleable casting showing decarburized rim. Magnified 100 diameters. (Boylston.)

ness of the core is due, as we now understand, to the transformation of cement carbon into temper carbon.

The annealing temperature for the production of black heart castings is generally between 700 and 800 deg. C. in the case of air furnace iron, that is, but slightly above the critical range of the metal, and the length of time at the full converting temperature between 2½ and 3 days. Moldenke states that cupola iron castings should be annealed at temperatures some 65 to 120 deg. higher and writes: [1]

"Just why there should be a difference in the temperature required for castings of the same composition when made in the cupola or in the air furnace, is one of the unsolved problems. It may be chemical in that the degree of oxidation has its effect on the opening up of the structure under the influence of heat. It may, on the other

[1] A. Lissner writes that in cupola metal containing 0.25 per cent sulphur, temper carbon begins to form at 760 deg. C.

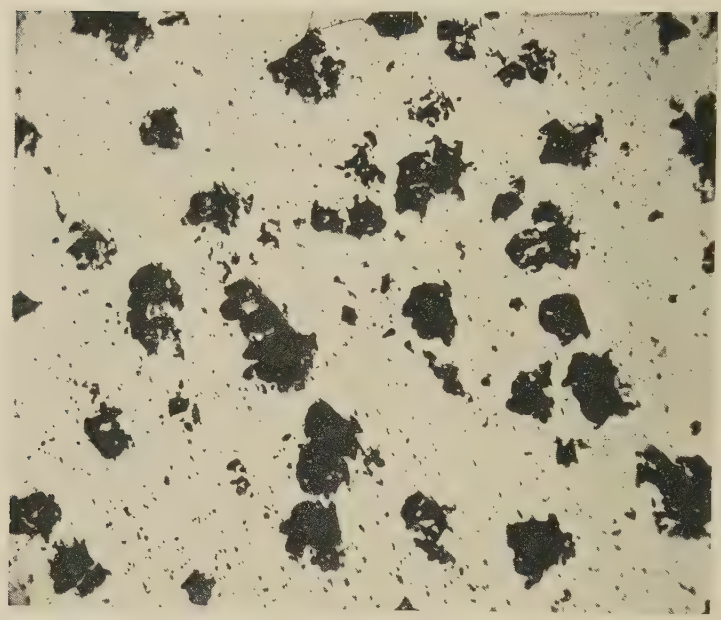


Fig. 355. — Black heart casting. Magnified 100 diameters. Not etched. (F. C. Langenberg, in the author's laboratory.)

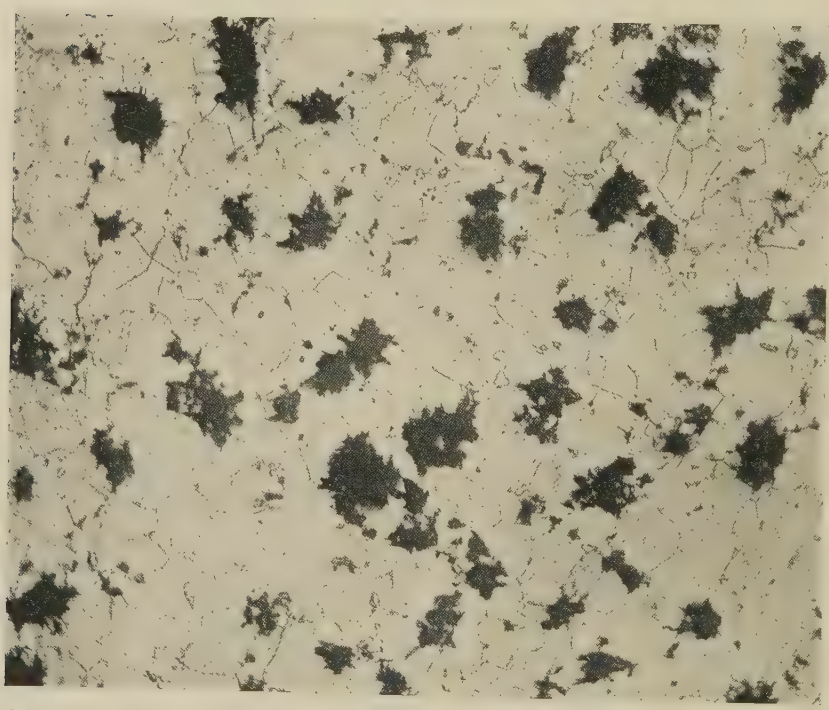


Fig. 356. — Black heart malleable casting. Magnified 100 diameters. Total carbon 2.64 per cent. Silicon 0.76 per cent. Phosphorus 0.137 per cent. Sulphur 0.031 per cent. Manganese 0.380 per cent. (Boylston.)

hand, be a matter of molecular physics, and depend on the constitution and structure of the castings as made, either in the contact of fuel with iron, or not. Possibly it

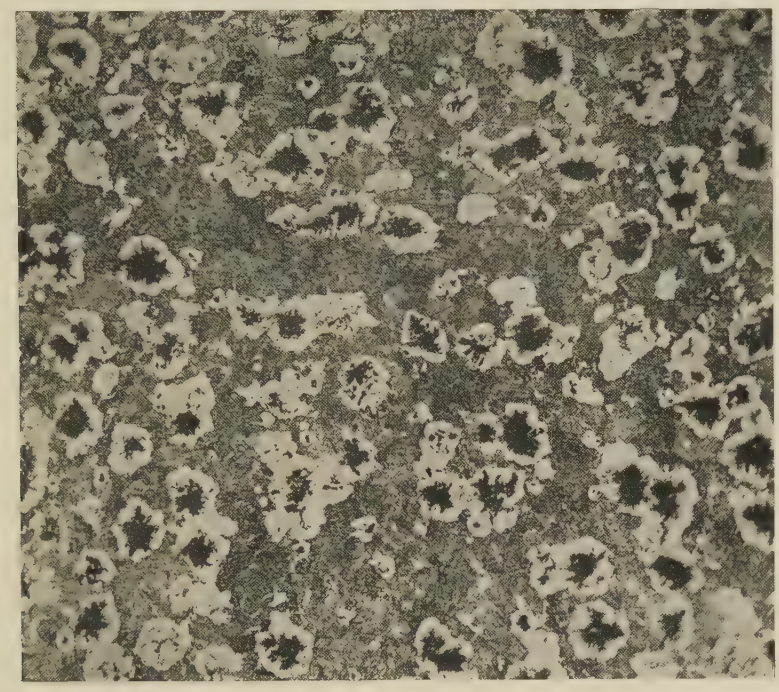


Fig. 357. — Partially malleablized cast iron. Magnified 100 diameters. Total carbon 2.55 per cent. Silicon 0.77 per cent. Phosphorus 0.164 per cent. (F. H. Franklin of Saunders and Franklin.)

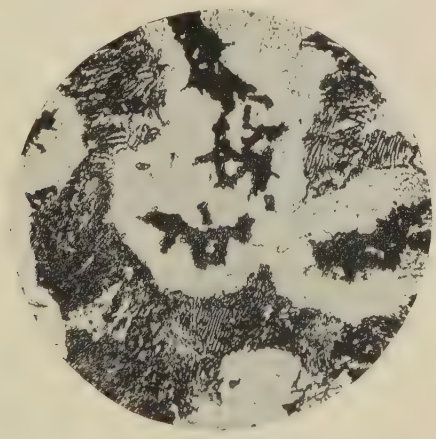


Fig. 358. — Partially malleablized cast iron. Magnified 500 diameters. (Wüst.)

may be a combination of both the chemical and the physical. Yet the problem still remains to be solved."

In completely malleablized black heart castings practically the whole of the carbon should be present in the graphitic condition, the castings consisting then of a

narrow case of decarburized iron and of a core made up of ferrite and particles of temper carbon, as shown in Figure 354. The structure of the core both before and after etching is further illustrated in Figures 355 and 356. If the malleablizing is but partial because of too low a temperature, too short a treatment, too little silicon, or for some other reason, considerable dissolved carbon may remain, which in cooling through the critical range will give rise to the formation of pearlite. The structure of such partially malleablized cast iron is illustrated in Figure 357. It will be seen to consist of graphitic carbon, pearlite, and ferrite. The mechanism of the formation of such structures is obvious. At the end of the annealing treatment the metal consisted of a mass of austenite in which were embedded a number of particles of temper carbon; on slow cooling through the range the hypo-eutectoid austenite rejected some free ferrite until, its composition reaching the eutectoid carbon ratio, it was converted into pearlite. It will be noted that the pearlitic areas which should indicate the location of the residual austenite are situated away from the temper carbon particles, the latter being surrounded by ferrite.

The annealing of white cast iron may be so incomplete as to retain so much dissolved carbon that in slow cooling free cementite as well as pearlite will be formed. In this case the austenite which existed above the range at the end of the annealing operation was hyper-eutectoid, that is, it contained more than 0.85 per cent, or thereabout, of dissolved carbon, and on cooling through the range, therefore, liberated some free cementite. It is evident that partially malleablized cast iron, that is cast iron still containing considerable combined carbon, cannot be so malleable as malleablized cast iron free from combined carbon, since its metallic matrix is necessarily less malleable.

Cooling from Annealing Temperature. — According to B. L. Leasman, the cooling from the annealing temperature to 1250 deg. F. (675 deg. C.) should be very slow (42 hours), while below it may be rapid.

Gray Cast Iron vs. Malleable Cast Iron. — From the foregoing description of the nature and manufacture of malleable cast-iron castings it is evident that gray cast iron and malleable cast iron may have exactly the same chemical composition, although, of course, the former will generally contain more silicon and total carbon. In spite of identical or nearly identical composition, however, these two metals differ enormously in physical properties, gray cast iron being weak and brittle, malleable cast iron much stronger, and endowed with remarkable shock-resisting qualities. To account for this we must look into the microstructure of both metals, when it will be observed that in gray cast iron the graphite occurs in large, generally curved, flakes and plates, whereas in malleable cast iron it is present in small rounded particles, and it may well be conceived that the mode of occurrence of graphite in gray iron breaks up the continuity of the metallic matrix much more effectively, therefore weakening it and destroying its ductility. Were it possible during the solidification of cast iron to cause the graphite to occur as it does in malleable cast iron, there is no reason to doubt but that it would be as strong and as ductile.

CHAPTER XXIV

CONSTITUTION OF METALLIC ALLOYS

For many years vague and conflicting opinions were entertained in regard to the nature of metallic alloys. It was not known whether these intimate associations of two or more metals were merely mechanical mixtures or chemical compounds, while the existence of solid solutions was unsuspected. The application to the study of metallic alloys of the determination of the solubility curves which had proved so fruitful in investigating the mechanism of the solidification of ordinary (liquid) solutions and of mixtures of melted salts, soon followed by the microscopical examination of their structure, have at last revealed their true constitution. We know now that metallic alloys may be considered as solutions of high freezing (solidification) point and, therefore, solid at ordinary temperature, whereas the old conception of solution applied only to substances liquid at that temperature. It is evident, however, that the location of the freezing point of a substance in the temperature scale can have no bearing whatever upon its constitution, that is, upon the mode of occurrence of its constituents and the nature of the bond uniting them.

In these chapters the constitution of metallic alloys will be considered only so far as necessary to understand the equilibrium diagram described in Chapter XXV in which steel and cast iron are considered as alloys of iron and carbon, i.e. as solutions of these elements, liquid at a very high temperature, frozen at ordinary temperature.

Since, moreover, steel and cast iron are considered as pure iron-carbon alloys, it will suffice for our purpose to deal only with alloys of two metals, that is with binary alloys.

The constitution of alloys is revealed chiefly (1) through the mechanism of their solidification, as disclosed by their "fusibility" curves, and (2) through the microscopical examination of their structure after solidification.

Solidification of Pure Metals. — Let us first consider the solidification of a pure metal by observing its rate of cooling from the molten to the solid condition. This involves the use of a pyrometer, preferably a thermo-electric (Le Chatelier) instrument, the hot junction of which, suitably protected, is embedded in the cooling metal. By recording the successive intervals of time in seconds required for each successive cooling through ranges of temperature say of 10 deg. C., and plotting time against temperature, a cooling curve of the type shown in Figure 359 is obtained.[1] The teachings of such curves are obvious. Starting with the molten metal at A, its temperature being T, its cooling from A to B, while its temperature is falling from T to Ts, is uniformly retarded. This results in the smooth, nearly straight portion AB of the curve. The cooling of a molten metal above its solidification point is in this respect similar to the cooling of any substance free from thermal critical points; the cooling curves

[1] Self-recording pyrometers may also be used.

obtained in such cases are always smooth curves, indicating a uniform increase in time as the temperature of the substance falls. The curve of Figure 359 indicates the occurrence of a sharp critical point at the temperature Ts corresponding to the horizontal portion BC of the curve. It is evident that on reaching Ts the temperature of the metal suddenly ceased to fall and remained stationary during an interval of

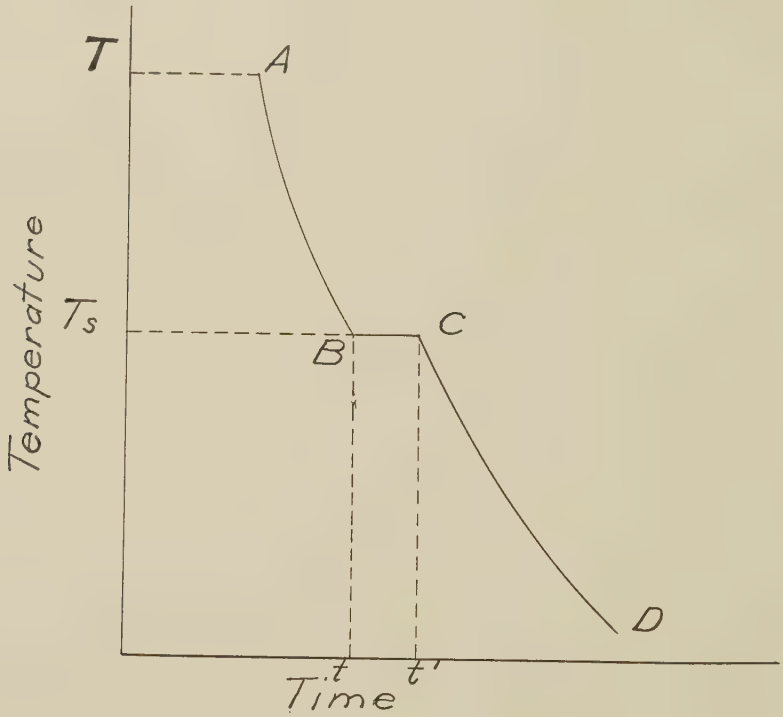


Fig. 359. — Typical cooling curve of pure metal.

time represented by $t'-t$. The metal then resumed a normal rate of cooling which was continued to atmospheric temperature, as indicated by the smooth portion CD which, were it not for the jog BC, would be a continuation of AB. We naturally connect this sudden appearance of a critical point in the cooling curve with the solidification of the metal. It clearly indicates (1) that the metal begins to solidify at the temperature Ts, (2) that while it is solidifying its temperature remains constant, (3) that the solidification lasts $t'-t$ seconds. It is evident that during its solidification the metal was exposed to the same cooling influences as those prevailing above and below it, and since its temperature nevertheless remains constant it must be that heat is here liberated in amount exactly sufficient to make up for the heat lost by radiation and conductivity. Any attempt at increasing the rate of cooling during solidification would result in hastening solidification and not in lowering the temperature of the metal. The heat evolved during the solidification of a substance is known as its "latent heat of solidification." In Figure 359, AB then represents the cooling of the liquid metal, BC its solidification, and CD the cooling of the solidified metal. On heating a pure metal from below to above its melting point, a similar curve is obtained, indicating (1) that the melting point coincides with the solidification point, at least under normal

conditions, and (2) that the melting takes place at a constant temperature, being, therefore, accompanied by an absorption of heat.

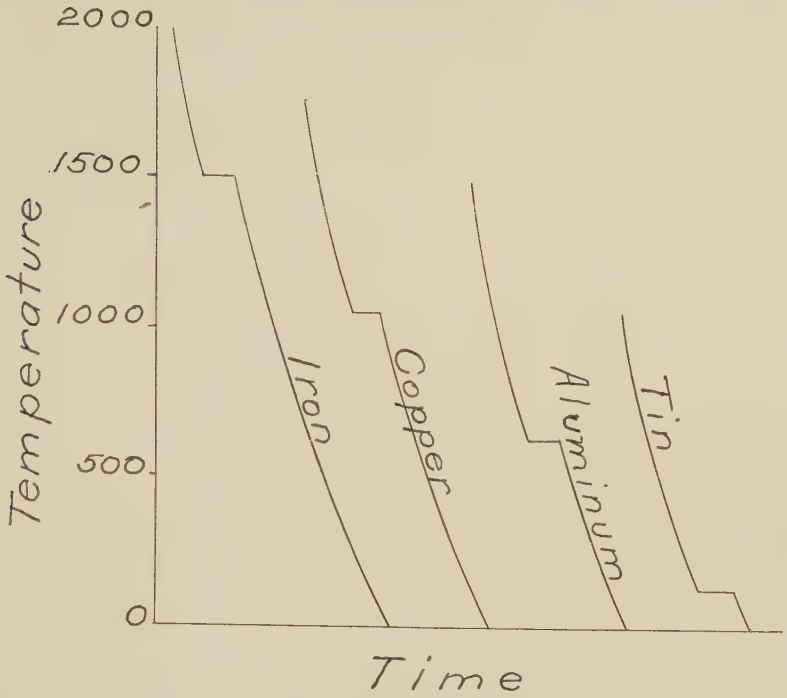


Fig. 360. — Cooling curves of various pure metals.

Fig. 361. — Pure lead. Magnified 20 diameters.
(F. C. Langenberg, in the author's laboratory.)

In Figure 360 the cooling curves of several pure metals are shown. They differ only in regard to the location of the horizontal portions indicating the temperatures of solidification.

The structure of pure metals has been described in Chapter I, when they were shown to be made up of polyhedral crystalline grains, each grain consisting of true crystals of uniform orientation. As an instance of the structure of pure metals, the structure of pure lead is shown in Figure 361.

Solidification of Binary Alloys the Constituents of which Form Solid Solutions. — The cooling or solidification curves of alloys of two or more metals may be constructed exactly like the cooling curve of a pure metal, namely, by observing the rate of cooling

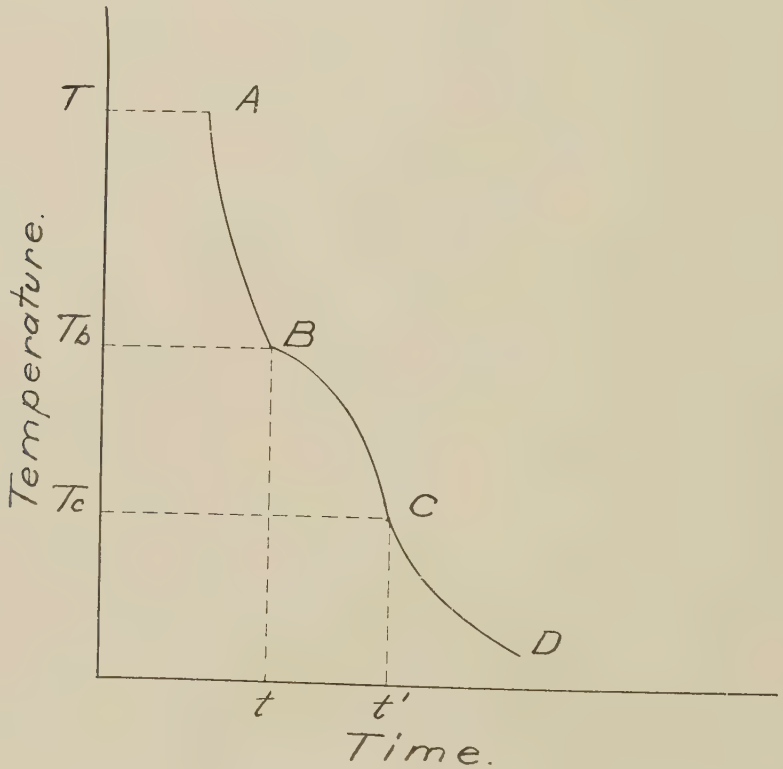


Fig. 362. — Typical cooling curve of binary alloy whose component metals form a solid solution.

as the temperature is lowered from above the melting point to atmospheric temperature and plotting the intervals of time against the corresponding temperature falls. A number of binary alloys are then found to yield cooling curves of the type shown in Figure 362. From A to B, that is as the alloy cools from T to Tb, the curve is smooth, and therefore indicative of normal cooling. At B there is a sudden change of direction, and from B to C, that is from the temperature Tb to the temperature Tc, the cooling of the alloy is evidently abnormally slow. From C to D, that is from the temperature Tc to atmospheric temperature, the cooling is again normal. Since the portion BC of the curve clearly indicates spontaneous evolutions of heat causing a marked retardation in the cooling of the alloy and lasting $t'-t$ seconds, we naturally infer that it corresponds to its solidification. It follows from the appearance of the cooling curve that alloys yielding such curves do not, like pure metals, solidify at a constant temperature but that their solidification, on the contrary, lasts $t'-t$ seconds while their

temperature falls from Tb to Tc. Summing up, AB indicates the cooling of the molten alloy, B the beginning, and C the end of its solidification, $t'-t$ the time required for its solidification, $Tb-Tc$ the fall of temperature during solidification, and CD the cooling of the solidified alloy. Above the point B, therefore, the alloy is entirely liquid, below C it is entirely solid, while between B and C it is partly liquid and partly solid. The point B is accordingly called the liquidus point and C the solidus point.

Binary alloys whose cooling curves are of the type shown in Figure 362 are known to be solid solutions. In these alloys the component metals which are completely merged in the liquid condition remain likewise so completely merged after solidification that their separate existence cannot be detected by microscopical examination or

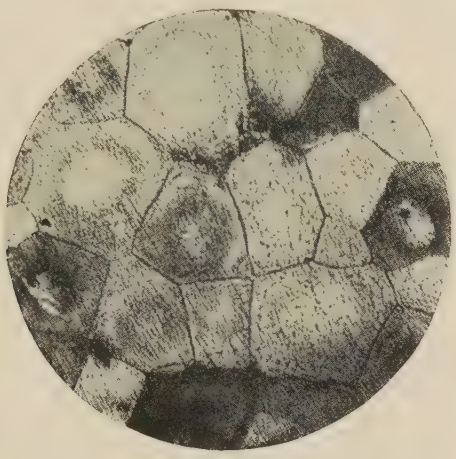


Fig. 363. — Copper-zinc alloy. Copper 50 per cent. Magnified 200 diameters. Solid solution. (Guillet.)

other physical means. They formed, on solidifying, homogeneous crystals containing both metals in indefinite proportions. These crystals are sometimes called "mixed crystals," and substances yielding them "isomorphous" mixtures, by which it is meant that only isomorphous substances [1] can yield mixed crystals, or in other words can form solid solutions. The expression "solid solution" is much preferable and is now quite universally used, at least by the English and French.

The mechanism of the formation of solid solutions of two metals should be examined more closely. Let us assume that a certain proportion of the metal M of relatively low melting point is alloyed with, or dissolved in, the metal M' of higher melting point. The metal M may be considered as the solute and M' as the solvent. It is believed that when solidification begins homogeneous crystals of M and M' are formed, but that they contain a smaller proportion of the fusible metal M than the liquid bath, which is thereby enriched in M.[2] On further cooling these crystals grow,

[1] Isomorphous substances are those that are capable of crystallizing in the same crystallographic forms.

[2] It is because the bath becomes richer in the more fusible metal M that its melting point is lowered, resulting in its solidification covering a considerable and falling range of temperature. If the crystals first formed had the same composition as the bath, solidification would take place at a constant temperature. Witness the solidification of pure metals, of eutectic alloys, and of chemical compounds: the solidifying metal having the same composition as the liquid from which it forms, solidification takes place at a constant temperature.

but the crystalline matter now deposited contains more of the metal M than the crystals first formed, although still less than the molten bath, which is further enriched in M and so on, the crystals growing through successive additions of crystalline matter containing increasing proportions of the dissolved and relatively fusible metal M, and approaching, therefore, although not reaching, the composition of the molten metal

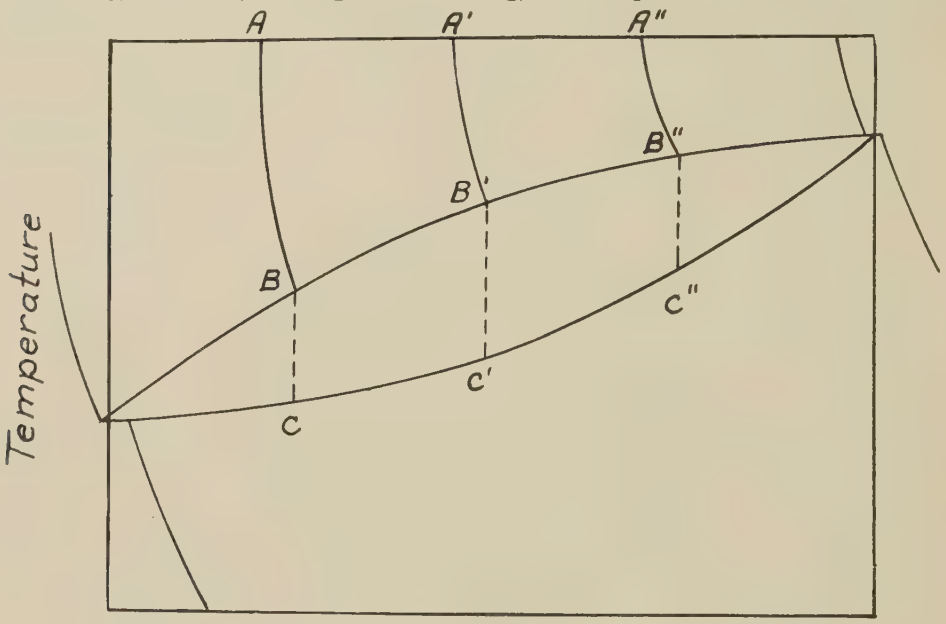


Fig. 364. — Diagram showing how fusibility curves are constructed.

until finally the last drop solidifies. Meanwhile, during solidification and as the temperature is lowered through and below the solidification range, diffusion takes place within the crystals so that finally they may become chemically homogeneous provided time be given (through slow cooling) for complete diffusion. Like pure metals, alloys whose component metals form solid solutions are composed of polyhedral crystalline grains (see Fig. 363).

Fusibility Curves of Binary Alloys whose Component Metals are Completely Soluble in Each Other when Solid. — So-called "fusibility curves" or "equilibrium diagrams" are obtained from any series of alloys by constructing the solidification curves, as explained above, of a number of alloys of that series and plotting on a single diagram the evolutions of heat observed. This has been done in Figure 364 by uniting the $BB'B''$ . . . and the $CC'C''$ . . . points denoting respectively the beginning and the end of the solidification of a number of alloys $AA'A''$ . . . Leaving out the independent cooling curves used for the construction of the fusibility curve, the diagram shown in Figure 365 is obtained, the co-ordinates being now temperature and composition. The figure is typical of the fusibility curves of binary alloys whose component metals are entirely soluble in each other when solid. They are composed of two branches, one concave the other convex, uniting the melting points of the constituent metals. MLM' is known as the liquidus because any alloy of the series above that line is entirely liquid, while MSM' is called the solidus because any alloy below it is entirely solid. Within the area $MLM'SM$ the alloys are partly liquid and partly solid. The solidification of these alloys should be further described with the help of

this diagram. Let us assume an alloy the composition of which is represented by the point P in the diagram and containing, therefore, 75 per cent of the low melting point metal M and 25 per cent of the less fusible metal M'. An alloy of that composition at the temperature T is entirely liquid since its condition is represented by a point situated above the liquidus. As the alloy cools from P to l its temperature falling from T to t, it still remains entirely liquid. At l, temperature t, solidification begins through the formation of crystals whose composition must be represented by

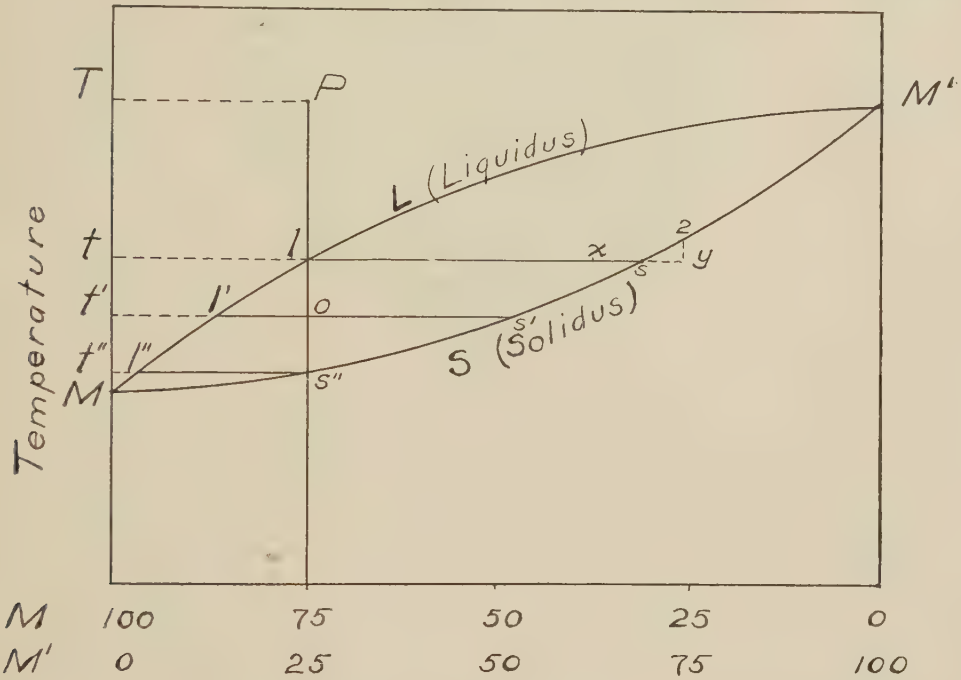


Fig. 365. — Typical fusibility curve of binary alloys whose component metals form solid solution.

the point s at the intersection of the solidus and of a horizontal line through l, for it is evident that the only crystals that can be in equilibrium at the temperature t with the liquid of composition l must have the composition s. To clarify, if the crystals in equilibrium with the liquid l at the temperature t have not the composition s, then they must necessarily contain either more of the metal M' or less of that metal. In other words, their composition may be represented by the point x to the left of s or by the point y to its right. It is evident that the composition of the crystals forming at the temperature t from a liquid of composition l cannot have the composition x since the corresponding point falls within the area $MLM'SM$ and since any point in this area cannot represent the composition of the crystals existing at the corresponding temperature but must represent on the contrary the *average* composition of the partly solidified alloy, hence the crystals forming at t in the case we are considering cannot have a composition represented by a point to the left of s. Assuming the composition of these crystals to be represented by the point y to the right of s, then it is evident that these crystals must have formed at z, that is, at a temperature considerably higher than t, which cannot be since our alloy does not begin to solidify before the temperature t is reached. Hence the composition of the crystals forming

at t, when the alloy P begins to solidify, cannot be represented by a point to the right of s. Clearly the point s must indicate the composition of those crystals. As the alloy cools from l to o, that is from t to t', the crystals which began to form at l con-

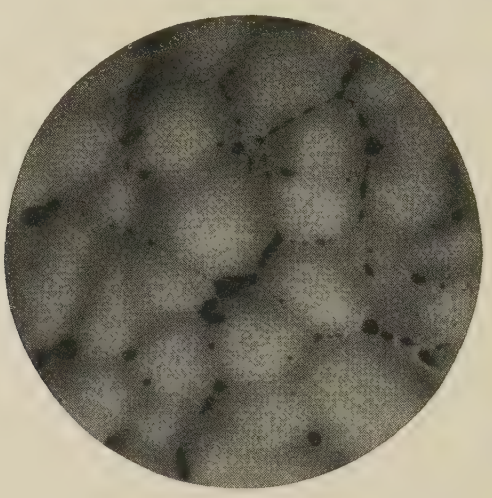


Fig. 366. — Iron-copper alloy. Copper 10 per cent. Magnified 125 diameters. Heterogeneous crystalline grains. The dark parts are richer in copper, the lighter parts richer in iron. (Stead.)

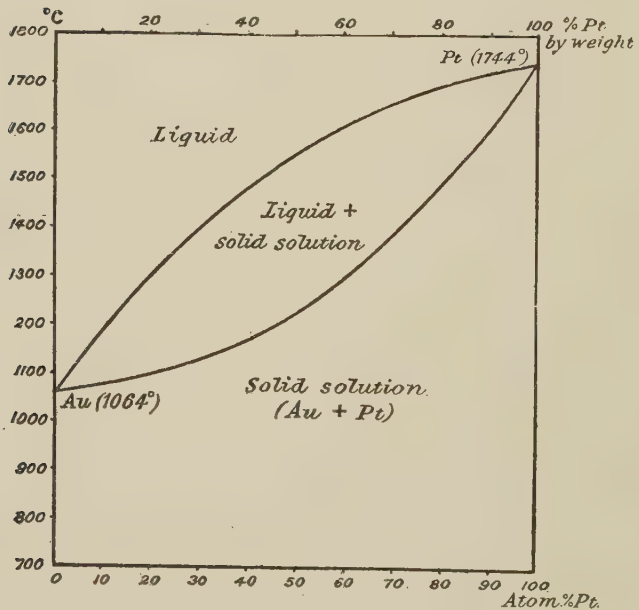


Fig. 367. — Fusibility curve alloys of gold and platinum. (Desch.)

tinue to grow by gradual deposition of crystalline matter progressively richer in M while the remaining liquid bath likewise becomes richer in M and consequently more fusible, its varying composition being represented by ll'. For any point o within the area $MLM'SM$, that is when the alloy is in the process of solidification, the com-

position of the crystals in equilibrium at the corresponding temperature t' with the solution l' is represented by the point s'. This must necessarily mean that as the metal cools from t to t' and while the crystals are growing, diffusion must necessarily take place in each crystal so that the concentric layers of varying composition of which we may conceive that they are initially composed, assume the same composition s', the crystals being now homogeneous. At s'', temperature t'', the solidification is complete. The last drop of liquid to solidify had the composition l''. By diffusion

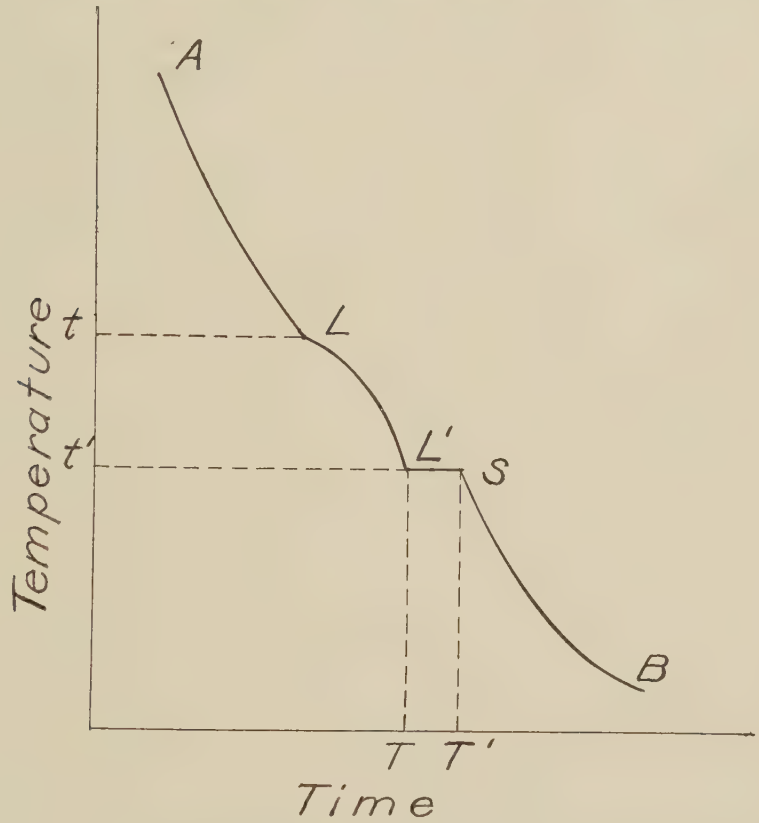


Fig. 368. — Typical cooling curve of binary alloy whose component metals are insoluble in each other in the solid state.

the crystals, which began to form at s and grew from s to s'', that is as the temperature fell from t to t'', have assumed a homogeneous chemical composition. While this diffusion, however, needed to produce homogeneous crystals readily takes place during the crystallization of liquid solutions, the case is different with solid solutions. Unless solidification and subsequent cooling have been sufficiently slow, solid solutions may remain heterogeneous, i.e. the different layers of crystalline matter of which each crystal is composed may not be of identical composition, the proportion of the most fusible metal increasing from center to outside (see Fig. 366). As an instance of binary alloys forming solid solutions the fusibility curve of gold-platinum alloys is reproduced in Figure 367.

Binary Alloys Forming Definite Compounds and Solid Solutions. — When two metals unite to form solid solutions, it does not necessarily imply that they may not

chemically combine with each other as well. Important instances are known of metals forming a definite chemical compound, which compound is then dissolved in the remaining excess metal. Two metals M and M', for instance, may unite chemically to form the compound $MxM'y$ and unless the alloy contains the two metals exactly in the required atomic proportions, the compound may form a solid solution with the excess of metal M or of metal M', as the case may be. In such cases the alloys should be considered not as alloys of two metals but of one metal and of one chemical compound of two metals, when the mechanism described to explain the solidification of solid solutions will be found applicable. Indeed we may conceive the existence of alloys of two metals in which two definite compounds are formed, mutually soluble and, therefore, forming solid solutions. Such alloys should be considered not as alloys of two pure metals but of two chemical compounds, the mechanism of their solidification being then identical to that of alloys of two metals.

Binary Alloys whose Component Metals are Insoluble in Each Other in the Solid State. — If two metals, although soluble in the liquid state, are insoluble when solid, it is evident that on solidification they must crystallize separately into distinct crystals readily distinguishable under the miscroscope, in other words, that the solid alloy must be an aggregate of the two metals. The study of the mechanism of the solidification of such alloys and of their microstructure should receive some attention.

The typical cooling or solidification curve of an alloy of two metals insoluble in each other when solid is shown in Figure 368. The curves are obtained, as previously explained, by observing the time required by the alloy to cool through successive and equal ranges of temperature and by plotting the times against the corresponding falls of temperature, or more conveniently and accurately by the use of self-registering pyrometers. The curve of Figure 368 will be seen to consist of four parts, namely, AL indicating a normal rate of cooling, LL' a retarded cooling, $L'S$ a stationary temperature, and SB a normal rate of cooling to atmospheric temperature. It is logical to infer that AL represents the uniform cooling of the liquid alloy and SB the uneventful cooling of the solid metal, L being the liquidus point and S the solidus. The portion of the curve $LL'S$ represents the solidification of the alloy as the temperature falls from t to t'. It will be observed (1) that the solidification begins at L, temperature t, (2) that it proceeds from L to L' as the *temperature is falling*, and (3) that the end of the solidification takes place at a *constant temperature*, namely, t', as indicated by the horizontal portion $L'S$, the temperature of the alloy remaining constant during $T' - T$ seconds.

In Figure 369 the solidification curves of a number of alloys of the same series have been constructed as explained above, the alloys arbitrarily selected containing respectively 10, 20, 40, 60, and 80 per cent of metal M. It will be noted that, with the exception of the alloy containing 40 per cent of M, each alloy exhibits two evolutions of heat, namely an upper evolution, L, at varying temperatures, and a lower, E, always at the same temperature regardless of the composition of the alloy. By uniting the upper points and the lower ones as indicated by dotted lines in Figure 369, the so-called fusibility curve or equilibrium diagram of that series of alloys is obtained. In Fig. 370 the fusibility curve only is represented, the independent cooling curves used for its construction having been omitted. The co-ordinates are now composition and temperature. The curve indicates clearly the beginning and the end of the solidification of any alloy of the series. The solidification of an alloy whose composition corresponds to the point R, for instance, and which therefore contains 20 per cent of metal M and

80 per cent of metal M', evidently begins at N and ends at P. The fusibility curve is made up of three branches, namely, the two intersecting lines LE and $L'E$, starting

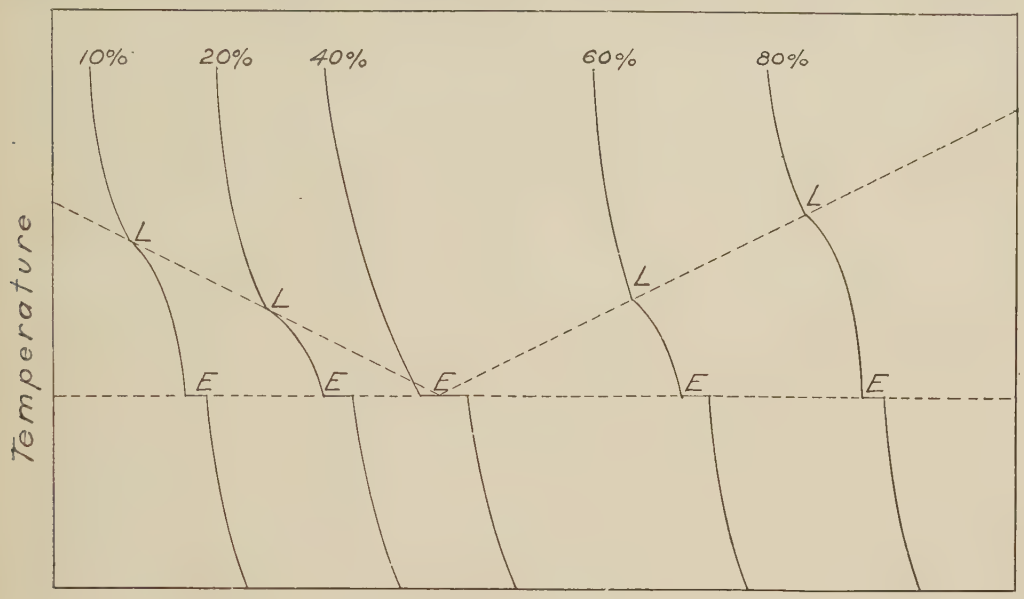


Fig. 369. — Diagram showing how fusibility curves are constructed.

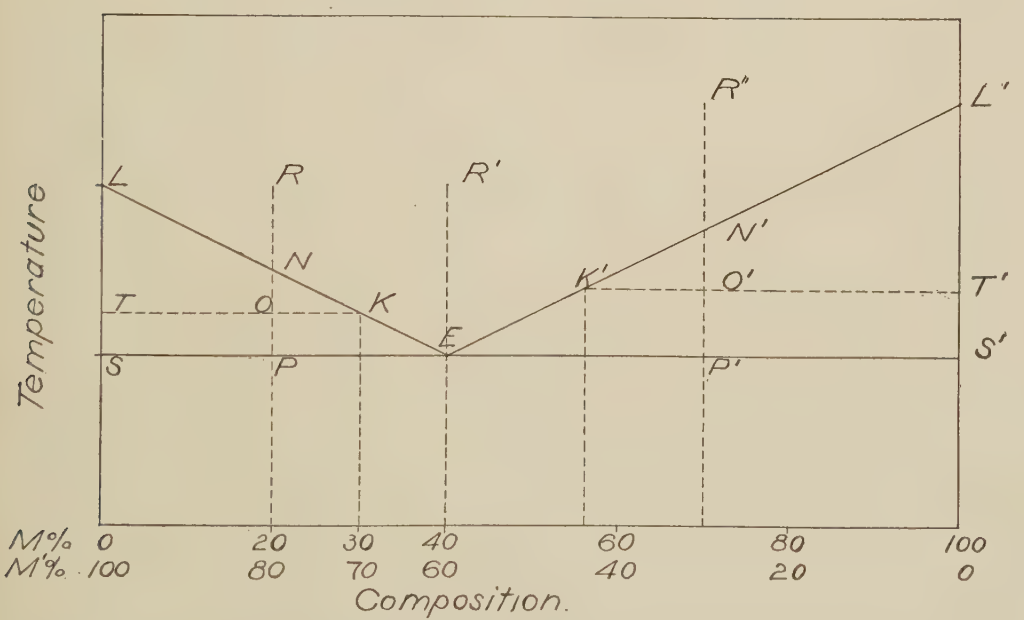


Fig. 370. — Typical fusibility curve of binary alloys whose component metals are insoluble in each other in the solid state.

respectively from the melting points of the two constituent metals and a horizontal line SS' passing by the point of intersection E of the first two. This is the typical fusibility curve of binary alloys whose component metals are insoluble in each other

in the solid condition. The solidification of these alloys should now be examined more closely. Several features are obvious. The different alloys *begin* to solidify at different temperatures according to their composition. At first, as the percentage of M increases from 0 to 40 (a proportion arbitrarily selected), the solidification point is lowered from L to E, while with further increase of M from 40 to 100 per cent, the solidification point is raised from E to L'. The solidification of all alloys, however, *ends* at the same temperature, namely, at the temperature S. Clearly, LEL' is the liquidus and SES' the solidus. The alloy containing 40 per cent of M is evidently the most fusible alloy of the series since it remains liquid until the temperature S is reached, while other alloys begin to solidify at higher temperatures. This alloy of lowest melting point is known as the "eutectic" alloy, from the Greek meaning "well melting." It is evident that, like pure metals, eutectic alloys solidify at a constant temperature, namely, the eutectic temperature. Many aqueous solutions also give rise to the formation of solutions of lowest freezing points called "cryohydrates" and which were at first supposed to be true chemical compounds, that is, hydrates containing salt and water molecules in atomic proportions. And, likewise, eutectic alloys were at first supposed to be definite chemical compounds of the two metals. They are now known to be aggregates of these metals generally very finely divided. This will be made clear by following the solidifications of three alloys, R, R', and R'' (Fig. 370). The alloy R contains, according to the diagram, 20 per cent of the metal M and 80 per cent of the metal M'. Since it contains less of the metal M than the eutectic alloy, we may for convenience refer to it as a hypo-eutectic alloy, although of course in regard to the content of M' it would be hyper-eutectic. In cooling from R to N the alloy remains liquid. At N solidification begins through the formation of pure crystals of M', that is, of the metal which is present in excess above the eutectic ratio. The formation of pure crystals of M' continues as the alloy cools from N to P, and meanwhile the portion of the alloy remaining liquid (we may call it the mother metal) becomes gradually richer in M, i.e. it approaches gradually the composition of the eutectic alloy. Finally at P, temperature S, the remaining liquid has exactly the eutectic composition and now solidifies at a constant temperature, the solidification temperature of the eutectic alloy. In other words, as the alloy cools from N to P with formation of pure crystals of metal M' the composition of the portion of the alloy remaining liquid varies according to the line NKE, reaching the composition E, that is the eutectic composition, always at the same temperature regardless of the initial composition of the alloy. When the alloy has cooled to O, for instance, a point between LE and SE, it is partly liquid and partly solid, its temperature is T, and the composition of the liquid portion is represented by K, that is it contains 30 per cent of the metal M. On further cooling from O to P the composition of the mother metal shifts from K to E.

In the case of the alloy R'', containing a larger proportion of the metal M than the eutectic alloy and which we may, therefore, consider to be hyper-eutectic, when it reaches the point N' its solidification begins, pure crystals of the metal M being formed, while the molten bath becomes gradually richer in M', gradually approaching, therefore, the composition of the eutectic alloy, until at the temperature S that composition is reached when the remaining liquid solidifies at a constant temperature. Any point O' situated between $L'E$ and $S'E$ indicates an alloy in part solid and in part liquid; its temperature is T' and the composition of the liquid is represented by K'. On cooling from O' to P' additional crystals of pure M are formed, or those

already formed continue to grow while the composition of the molten metal shifts from K' to E.

Starting with the alloy R' of eutectic composition, it remains liquid until at E, temperature S, it solidifies at a constant temperature, there being no excess metal to be rejected.

Seeing that the branch LE corresponds to the formation of pure crystals of the metal M' and the branch $L'E$ to the formation of pure crystals of the metal M, the

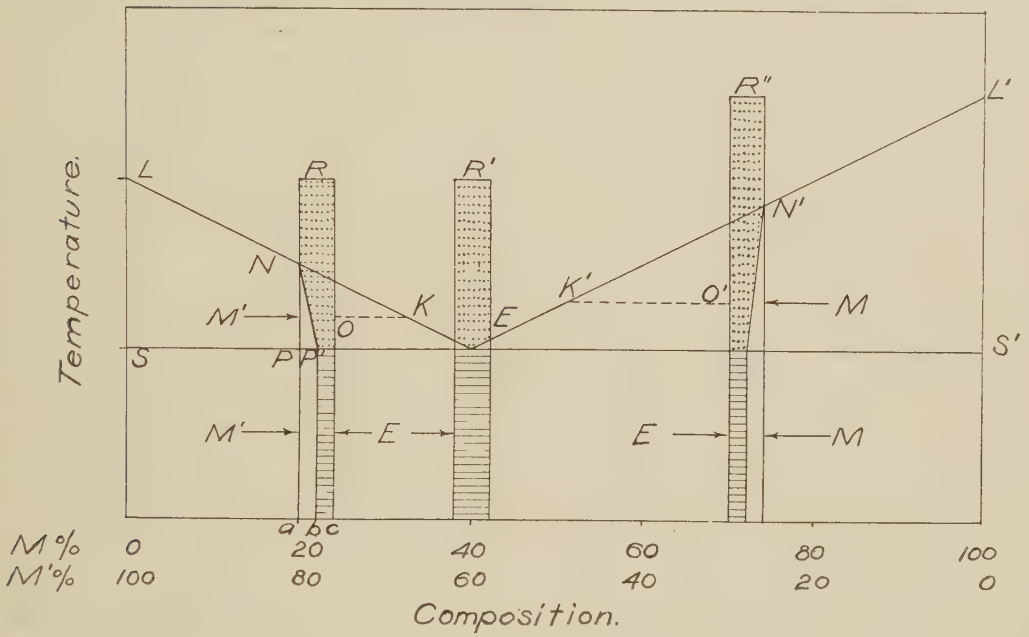


Fig. 371. — Diagram depicting the mechanism of the solidification of alloys whose component metals are insoluble in each other in the solid state.

conclusion seems irresistible that their point of intersection E must correspond to the simultaneous formation of crystals of metal M and of metal M' and that the eutectic alloy, therefore, must be a finely divided aggregate of M and M'. In other words, at any point on the branch LE, the alloy is saturated with the metal M' so that the lowering of its temperature must cause the separation of M' crystals with corresponding lowering of the saturation point, that is, of the solidification point of the bath. In a similar way, at any point on the branch $L'E$, the alloy is saturated with M and a fall in its temperature must result in the formation of M crystals, while the solidification point of the portion remaining liquid is thereby lowered. At E the alloy is saturated with both metals so that any attempt at lowering its temperature must result in the simultaneous deposition of crystals of M and of M', and since the composition of the bath remains the same, solidification now takes place at a constant temperature. Hence the constitution of eutectic alloys and the reason for their constant freezing temperature.

It has been attempted in Figure 371 to depict graphically the mechanism of the solidification of hypo-eutectic, eutectic, and hyper-eutectic alloys. As diagrams of this kind have already been used in these pages, the present one will be readily understood.

When the alloy R, for instance, reaches the point N, crystals of M' form, their

formation as the metal cools from N to P being represented by the area NPP'. At P the residual liquid, now of eutectic composition, solidifies at a constant temperature. At any point O the composition of the portion still liquid is represented by K. The

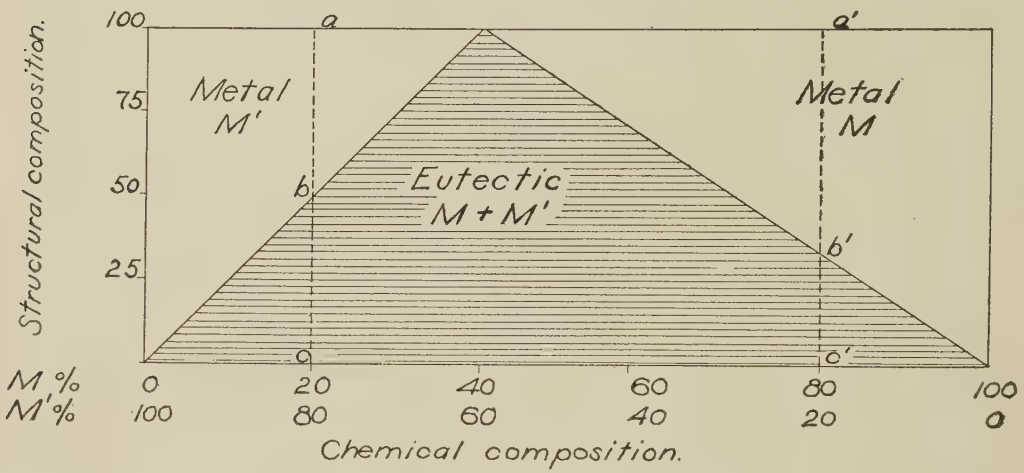


Fig. 372. — Diagram showing the structural composition of binary alloys whose component metals are insoluble in each other in the solid state.

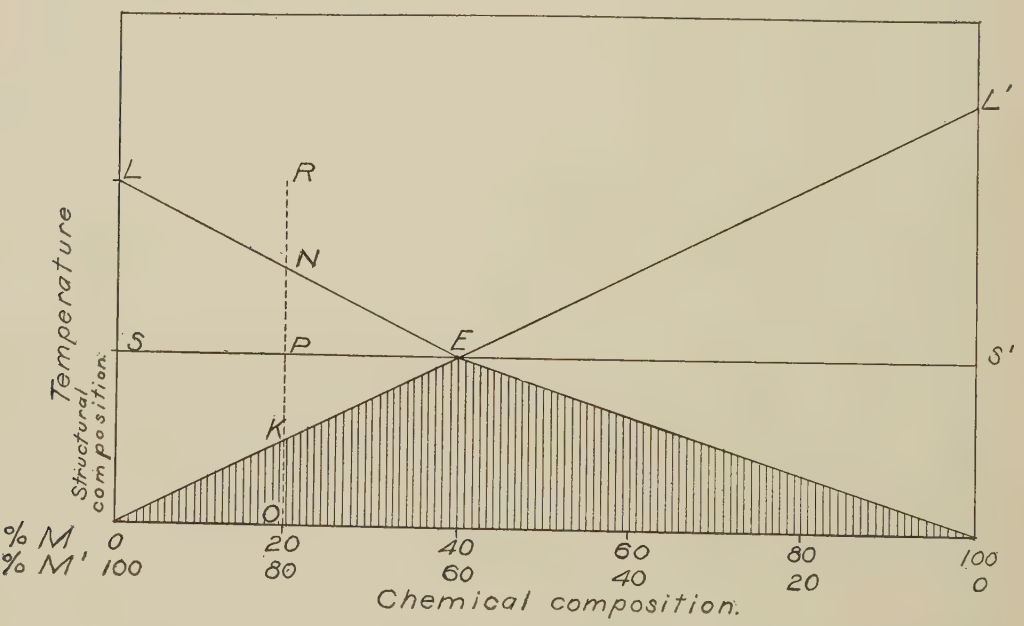


Fig. 373. — Diagram showing the fusibility curve and the structural composition of binary alloys whose component metals are insoluble in each other in the solid state.

completely solidified metal will be made up of ab per cent of metal M and bc per cent of eutectic alloy.

It will not be necessary to describe at greater length the graphical representation of the solidification of the alloys R' and R''.

The structural composition of alloys of two metals completely insoluble in each

other in the solid condition may conveniently be represented graphically as shown in Figure 372. The interpretation of this diagram is obvious. An alloy containing 20 per cent of the metal M, for instance, will be made up of ab per cent of M' and bc per cent of eutectic alloy. With 40 per cent of M the alloy is wholly of eutectic composition, while with 80 per cent of M, for instance, it contains $a'b'$ of M crystals and $b'c'$ per cent of eutectic.

The composition diagram may with advantage be combined with the equilibrium diagram as it has been done in Figure 373. Taking an alloy whose composition is represented by R, for instance (20 per cent M and 80 per cent M'), it is seen (1) that it begins to solidify at N, (2) that as it cools from K to P pure crystals of M' are formed, (3) that the percentage of M' thus liberated is represented by PK, (4) that

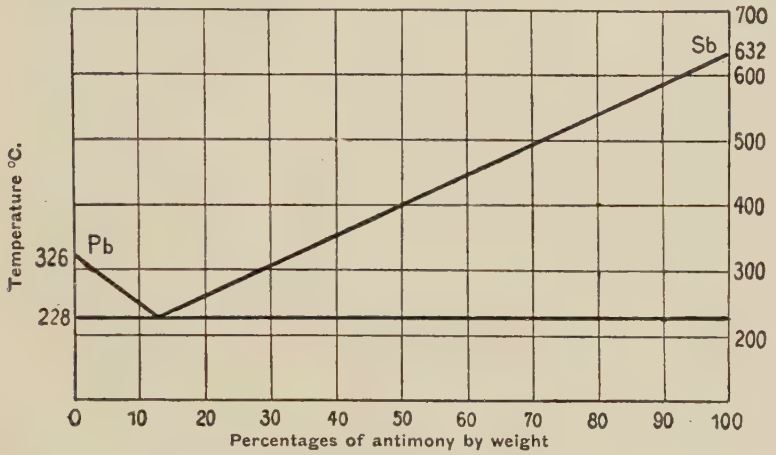


Fig. 374. — Fusibility curve of alloys of lead and antimony. (Roland-Gosselin.)

at P the remaining molten alloy now of eutectic composition solidifies, and (5) that KO represents the percentage of this eutectic alloy.

The graphical method used in these chapters for representing the structural composition of alloys was first suggested by the author in 1896. It has since been widely used and Tammann employs it to represent the heat liberated by the solidification of the eutectic or the time taken for its solidification, it being evident that both heat and time must necessarily be proportional to the *amount* of eutectic alloy formed. In Fig. 373, therefore, the vertical distances of the shaded area are proportional to the times during which the temperature of the alloys remained constant while the residual baths of eutectic composition were solidifying. The fusibility curve of lead-antimony alloys is reproduced in Figure 374 as an instance of alloys whose component metals are entirely insoluble in each other after solidification.

From the foregoing it appears that solidified alloys of two metals insoluble in each other are aggregates of these two metals and that three types of structure are to be expected: (1) the structure of hypo-eutectic alloys composed of crystals or crystalline grains or particles of one metal embedded in, or surrounded by, some eutectic alloy, (2) the structure of hyper-eutectic alloys consisting of crystalline particles of the other metal and of eutectic alloy, and (3) the structure of eutectic alloys consisting of a finely divided aggregate of minute particles of both metals. These three types are represented diagrammatically in Figure 375. Eutectic alloys are often made up of

very thin alternate and parallel plates or lamellæ of each of the two constituents, but in some cases they consist of rounded or elongated particles of one of the con-

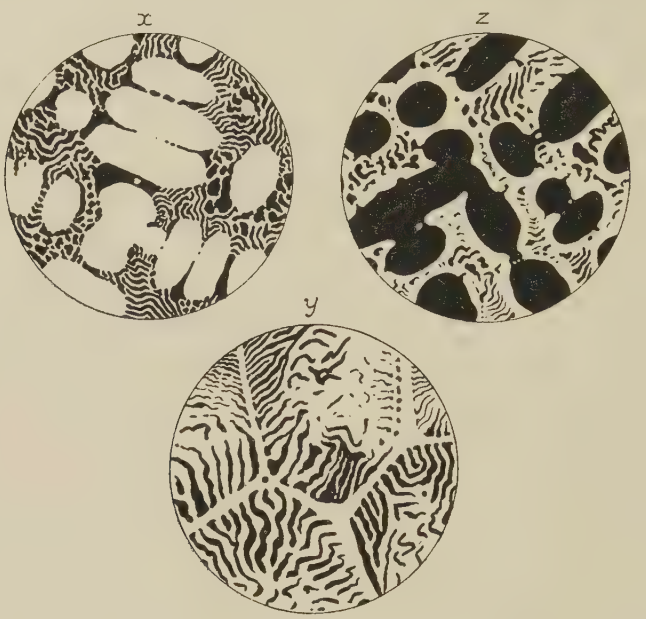


Fig. 375. — Typical structures of alloys whose component metals are insoluble in each other in the solid state. *x*, excess metal *M'* and eutectic; *y*, eutectic; *z*, excess metal *M* and eutectic. (Gulliver.)

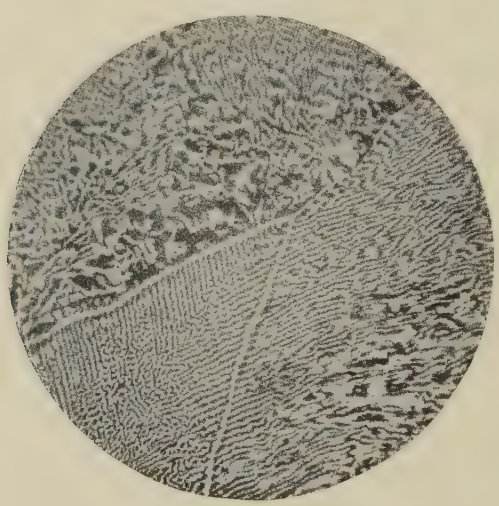


Fig. 376. — Eutectic alloy of bismuth and tin. Magnified 200 diameters. (Desch.)

stituents embedded in a matrix of the other constituents. The structures of some eutectic alloys are shown in Figures 376 to 378. It will be noted that the constituents of eutectic alloys are not always pure metals.

Binary Alloys whose Component Metals are Partially Soluble in Each Other when Solid. — Metals are seldom absolutely insoluble in each other when solid, each metal in the majority of cases being capable of retaining in solid solution a small percentage

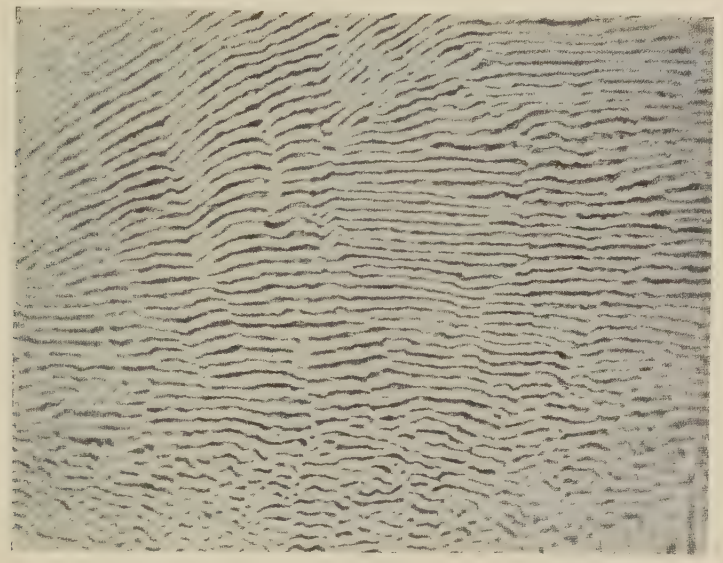


Fig. 377. — Eutectic (eutectoid) alloy of iron and Fe_3C. Pearlite. Magnified 1000 diameters. (Law.)

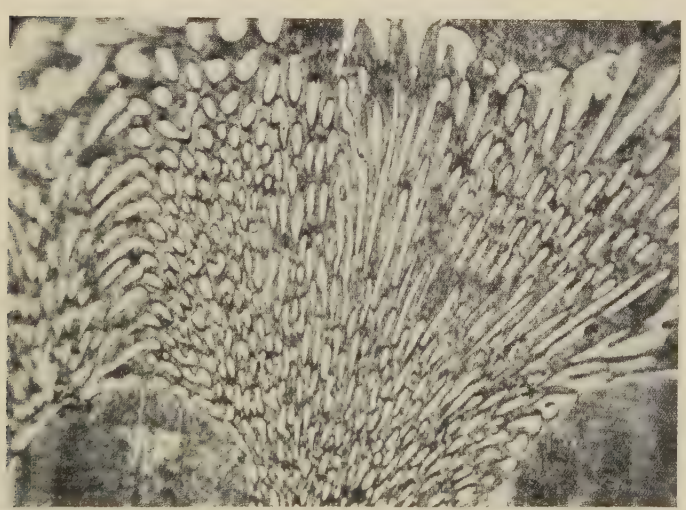


Fig. 378. — Eutectic alloy of $SnCu_4$ and Cu_3P. Magnified 1000 diameters. (Law.)

of the other metal. The modifications which such partial solubility introduces in the fusibility curve should be considered. Let us suppose two metals M and M' and let us assume that the metal M' is capable of retaining in solution immediately after solidification, i.e. at the eutectic temperature, 5 per cent of the metal M and that the metal M can retain in solid solution 10 per cent of the metal M'. The fusibility curve

of these alloys constructed in the usual way will have the appearance indicated in Figure 379. By comparing it with the fusibility curve of metals entirely insoluble (Fig. 370) it will be noted that the only differences between them are (1) that the eutectic line SES' instead of extending over the whole length of the diagram now stops at the points S and S', corresponding respectively to 5 per cent of metal M and

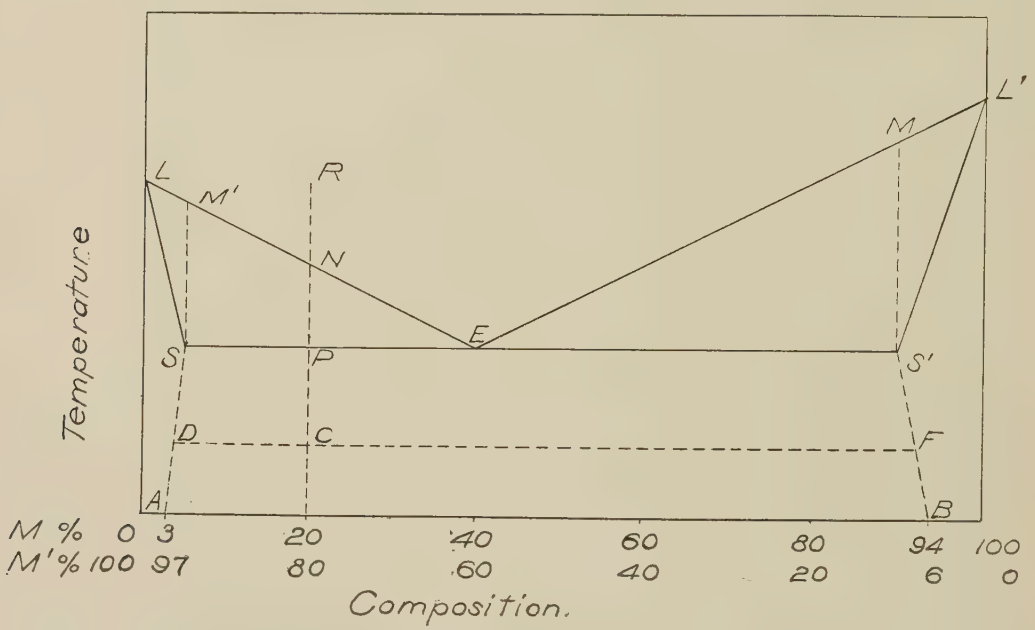


Fig. 379. — Typical fusibility curve of alloys whose component metals are partially soluble in each other in the solid state.

to 10 per cent of metal M', and (2) the introduction of the branches SA and $S'B$ indicates the changes of solubility of the metals as the alloys cool from the eutectic to atmospheric temperature. These curves show that at atmospheric temperature M' retains in solution 3 per cent of M and that M retains in solution 6 per cent of M'. LEL' is the liquidus, $LSES'L'$ the solidus. Clearly, any alloy containing less than 5 per cent of the metal M or less than 10 per cent of the metal M' solidifies as a solid solution, the diagram showing the absence of eutectic alloys. In other words, alloys containing from 0 to 5 per cent of M may be considered as alloys of M' and of a solid solution of M' plus 5 per cent of M, LM' being the liquidus and LS the solidus of such alloys and their solidification taking place as explained in the case of any two metals forming solid solutions. And, likewise, alloys with less than 10 per cent of M' may be regarded as alloys of the metal M and of a solid solution of M plus 10 per cent of M', their liquidus being represented by $L'M$ and their solidus by $L'S'$. For all alloys containing between 5 and 90 per cent of M the diagram shows that a eutectic alloy is formed and that the mechanism of the solidification is apparently the same as the one described in the case of alloys of insoluble metals. It should be noted, however, that the two components of these alloys are no longer the pure metals but two solid solutions, namely, a solution of M' containing 5 per cent of M and a solution of M containing 10 per cent of M', one of these solid solutions, therefore, crystallizing when the temperature of the alloy reaches any point on the lines LEL' and the eu-

tectic alloy being made up of a fine conglomerate of these two solid solutions. To clarify, let us consider an alloy represented by the point R, Figure 379. At N its solidification begins, crystals of a solid solution of M' containing 5 per cent of M being formed. At P the residual molten mass, having reached the eutectic ratio, crystallizes at a constant temperature as a fine aggregate of the two solid solutions. Since

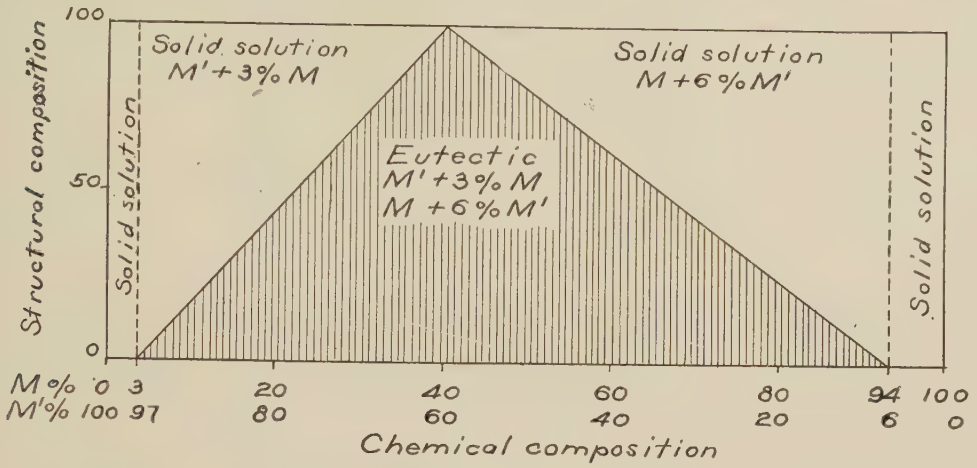


Fig. 380. — Diagram showing the structural composition of binary alloys whose component metals are partially soluble in each other in the solid state.

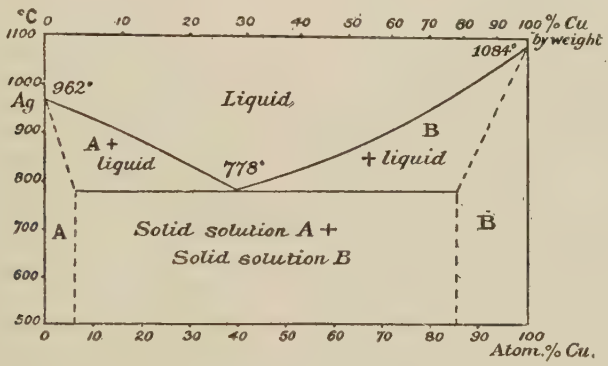


Fig. 381. — Fusibility curve of alloys of silver and copper. (Desch.)

the mutual solubilities of the metals M and M' decrease, however, as the alloy cools below the eutectic temperature, it is evident that each crystal must undergo a gradual transformation. These transformations are indicated by the branches SA and $S'B$. After the solidification of the eutectic, all alloys are aggregates of the two solid solutions whose compositions are represented by the points S and S', that is, in the case under consideration, arbitrarily, M' plus 5 per cent of M and M plus 10 per cent of M'. At atmospheric temperature all alloys are aggregates of two solid solutions whose compositions correspond to the points A and B, that is in the case considered M' plus 3 per cent of M and M plus 6 per cent of M'. At any point below the eutectic line, the corresponding alloy is an aggregate of two solid solutions whose compositions are indicated by the corresponding points on the branches SA and $S'B$. At C, for

instance, in case of alloy R, the structure is composed of free crystals of solid solution D and of eutectic, the components of which are solid solution D and solid solution F. In other words, as the alloy cools from the eutectic line to atmospheric temperature,

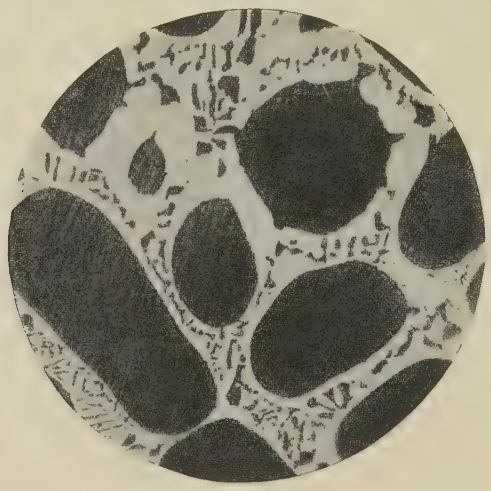


Fig. 382. — Silver-copper alloy. Copper 15 per cent. Magnified 600 diameters. Dark constituent is silver containing a little copper. (Osmond.)

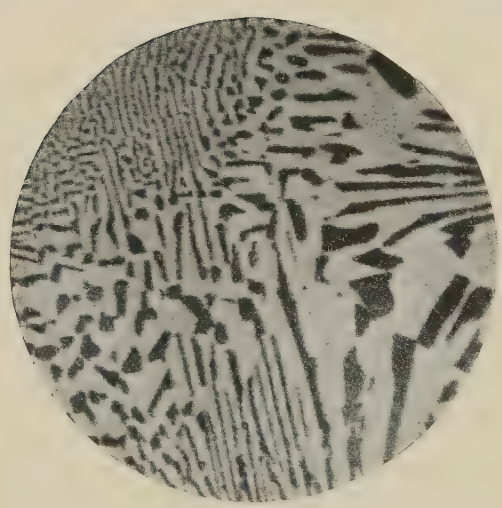


Fig. 383. — Silver-copper alloy eutectic. Copper 28 per cent. Magnified 600 diameters. (Osmond.)

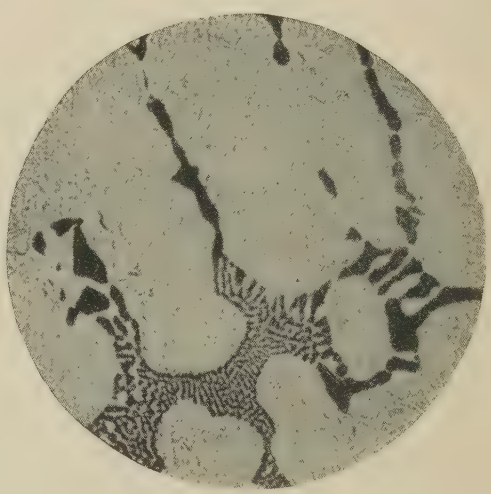


Fig. 384. — Silver-copper alloy. Copper 65 per cent. Magnified 600 diameters. Light constituent is copper containing a little silver. (Osmond.)

the composition of its two constituents shifts respectively from S to A and from S' to B.

The structural composition of alloys whose component metals are partially soluble when solid may be represented in the usual way as shown in Figure 380. Its interpretation does not call for further elaboration. Between 0 and 3 per cent of M and between 0 and 6 per cent of M', solid solutions are formed of corresponding com-

positions. Between 3 and 40 per cent of M, the free solid solution formed is saturated with M, and between 40 and 94 per cent of M it is saturated with M', while the eutectic is made up of the two saturated solutions. The fusibility curve of silver-copper alloys is shown in Figure 381 as an example of alloys whose components remain partly soluble in each other after solidification and typical structures of these alloys are given in Figures 382 to 384.

CHAPTER XXV

EQUILIBRIUM DIAGRAM OF IRON-CARBON ALLOYS

Fusibility Curve of Iron-Carbon Alloys. — Steel and cast iron are essentially alloys of iron and carbon, and their fusibility curve or equilibrium diagram may be constructed as in the case of any binary alloy, namely, by determining the independent cooling curves of a number of alloys of the series and plotting the evolutions of heat

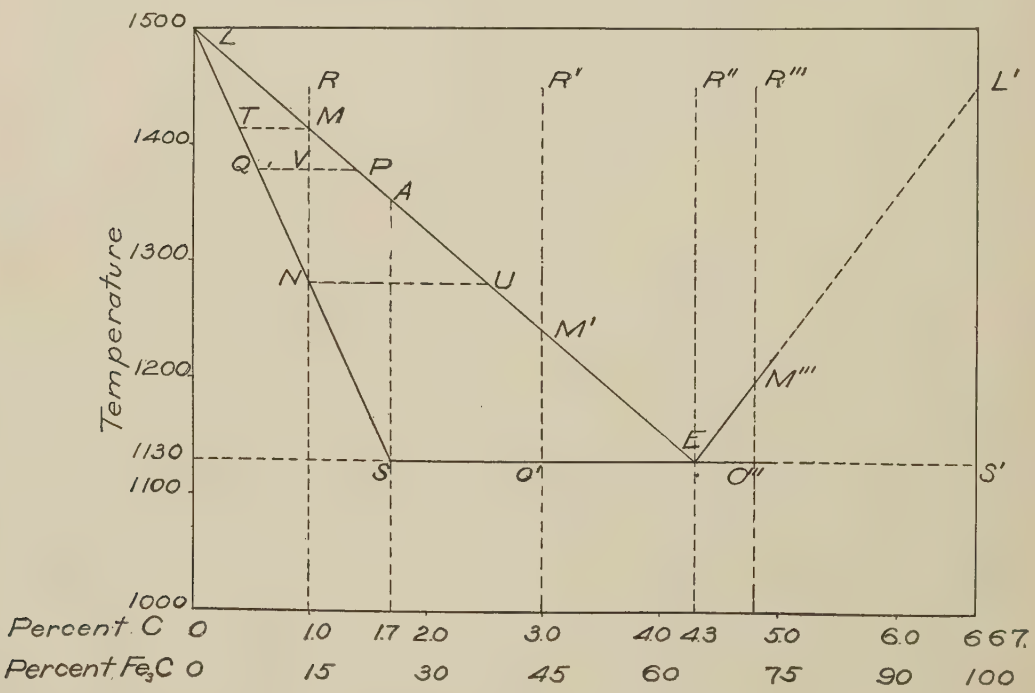


Fig. 385. — Fusibility curve of iron-carbon alloys.

noted against the corresponding temperatures. The resulting curve is shown in the diagram of Figure 385.

While it is not generally possible for molten iron slightly above its melting point to dissolve more than 5 per cent of carbon, the diagram has been constructed so as to include a percentage of carbon up to 6.67 per cent which corresponds to 100 per cent Fe_3C. That portion of it, however, corresponding to more than 5 per cent of carbon has been drawn in dotted lines. The complete equilibrium diagram should include the evolutions of heat occurring after solidification, known as the critical points, which have been fully described in these chapters, but they are purposely left out of

the diagram of Figure 385, it being desired first to confine our attention to the mechanism of the *solidification* of iron-carbon alloys. In view of the explanation of the meaning of fusibility curves given in Chapter XXIV, it will be evident that iron and carbon alloys are partially soluble in each other when solid, that LEL' is their liquidus and LSS' their solidus and that the point E indicates the formation of a eutectic alloy. As carbon increases from 0 to about 1.70 per cent, the alloys solidify as solid solutions of corresponding carbon content, LA being the liquidus and LS the solidus. These

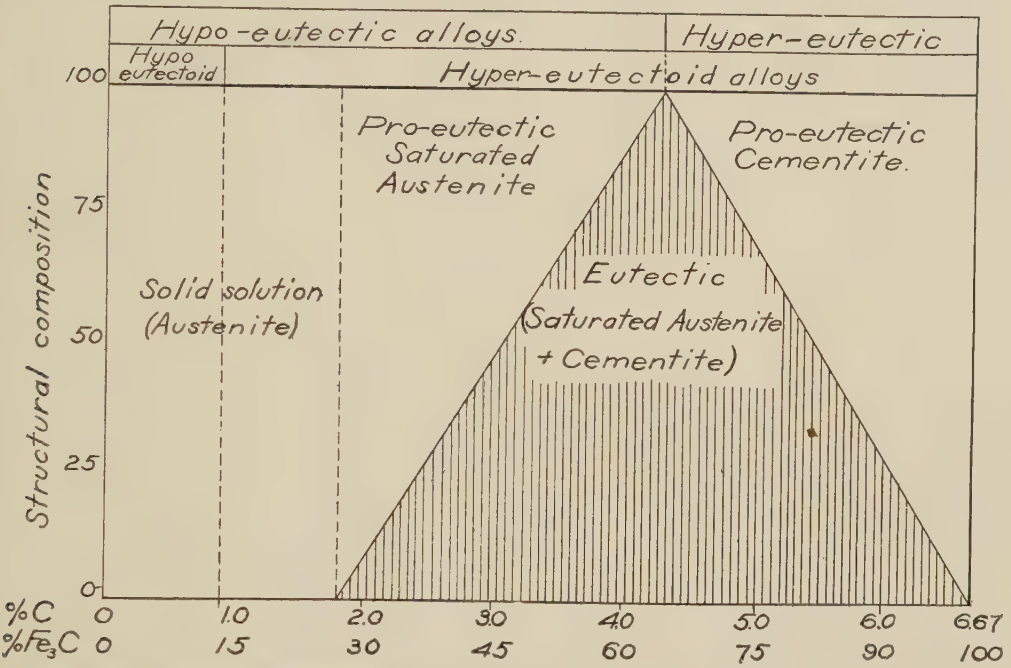


Fig. 386. — Structural composition of iron-carbon alloys immediately after their solidification.

solid solutions considered as microscopical constituents are called austenite. The solidification of alloys containing between 1.7 and 4.3 per cent carbon begins when their temperature reaches the line LE, crystals of a solid solution finally containing 1.70 per cent carbon (then called saturated austenite) being formed, which keep on growing until the line SS', temperature 1130 deg., is reached when, clearly, a eutectic is formed composed of that solid solution and of another constituent. The nature of the other constituent present in the eutectic alloy formed during the solidification of iron-carbon alloys has been in dispute. It seems at first natural to infer that elemental carbon, i.e. graphite, is that constituent, in which case the eutectic alloy would be made up of minute crystalline particles alternately of saturated austenite and of graphite. Many evidences, however, point to carbon being dissolved in molten iron as the carbide Fe_3C (cementite) and to its always solidifying as Fe_3C, although, as later explained, it may break up into iron and graphite ($Fe_3C = 3\,Fe + C$) immediately after its solidification. If this hypothesis be correct, it follows that the eutectic alloy must be a mechanical mixture of minute particles of saturated austenite and of Fe_3C. It would seem at first as if the microscopical examination of alloys of suitable compositions should readily reveal the nature of the eutectic alloy. It will soon be seen, however, that both cementite and graphite are generally found in solidified

eutectiferous alloys, the microscopical test leaving us in doubt as to which of the two constituents formed first. In the author's opinion it seems more probable that when an iron-carbon alloy containing more than some 1.70 per cent carbon solidifies, a eutectic of saturated austenite and of cementite is always produced, or in other words, that in the diagram of Figure 385 the curve $L'E$ indicates the crystallization of cementite and not of graphite. The opposite view will be considered later. Let us now follow the solidification of four typical alloys, namely, R, R', R'', R''', containing respectively 1 per cent, 3 per cent, 4.3 per cent, and 4.8 per cent of carbon, the first two being, therefore, hypo-eutectic alloys, the third the eutectic alloy, and the fourth a hyper-eutectic alloy. As the alloy R cools, it begins to solidify at M through the formation of crystals of a solid solution the composition of which is represented by the point T on the solidus. On cooling from M to N these crystals grow through successive additions of crystalline matter, the composition of which varies from T to N while the composition of the molten bath shifts from M to U, the last drop solidifying having the composition U. As soon as the crystalline matter is deposited, however, at least if time be given, diffusion takes place through the crystals so that finally they are chemically homogeneous and of composition N, the completely solidified metal being composed of homogeneous crystalline grains of austenite containing one per cent carbon.

At any temperature V between the solidus and the liquidus the crystals in equilibrium with the molten metal must have the composition Q. It may at least be conceived that if the cooling through and below the solidification period be rapid, the crystalline grains of austenite will not be chemically homogeneous, complete diffusion having been prevented.

In the case of an alloy whose composition is represented by the point R' in the diagram, it begins to solidify at M' (some 1230 deg. C.), when crystals of iron containing carbon in increasing proportions up to 1.70 per cent begin to form, the composition of the molten metal meanwhile shifting from M' to E. At O', temperature 1130, the residual molten mass has reached the eutectic composition and now solidifies at a constant temperature, namely, the eutectic temperature, the completely solid metal being made up of crystalline grains of saturated austenite surrounded by a eutectic alloy composed of minute crystals of saturated austenite and minute crystals of cementite.

The alloy R'' has the eutectic composition (4.3 per cent carbon). It remains liquid until its temperature falls to 1130 deg. C., when it solidifies at a constant temperature after the fashion of eutectic alloys.

The alloy R''' contains more carbon than the eutectic alloy. On reaching its solidification point M''' crystals of cementite begin to form, increasing in size as the metal cools from M''' to O''' while the composition of the bath shifts from M''' to E. At O''' the residual molten mass, having now the composition of the eutectic alloy, freezes at a constant temperature, the completely solidified alloy being made up of crystals of cementite embedded in a ground mass consisting of the eutectic alloy.

Structural Composition of Iron-Carbon Alloys Immediately after Solidification. — The structural composition of iron-carbon alloys *immediately after their solidification*, assuming that Fe_3C and not graphite forms, may be represented in the usual way by the diagram of Figure 386. The diagram clearly shows (1) that alloys containing less than 1.70 per cent of carbon are made up wholly of solid solutions, (2) that alloys containing between 1.70 and 4.3 per cent carbon are made up of decreasing proportions of saturated austenite and increasing proportions of eutectic, (3) that alloys

containing exactly 4.3 per cent of carbon are composed entirely of eutectic, and (4) that alloys containing more than 4.3 per cent carbon contain an increasing amount of

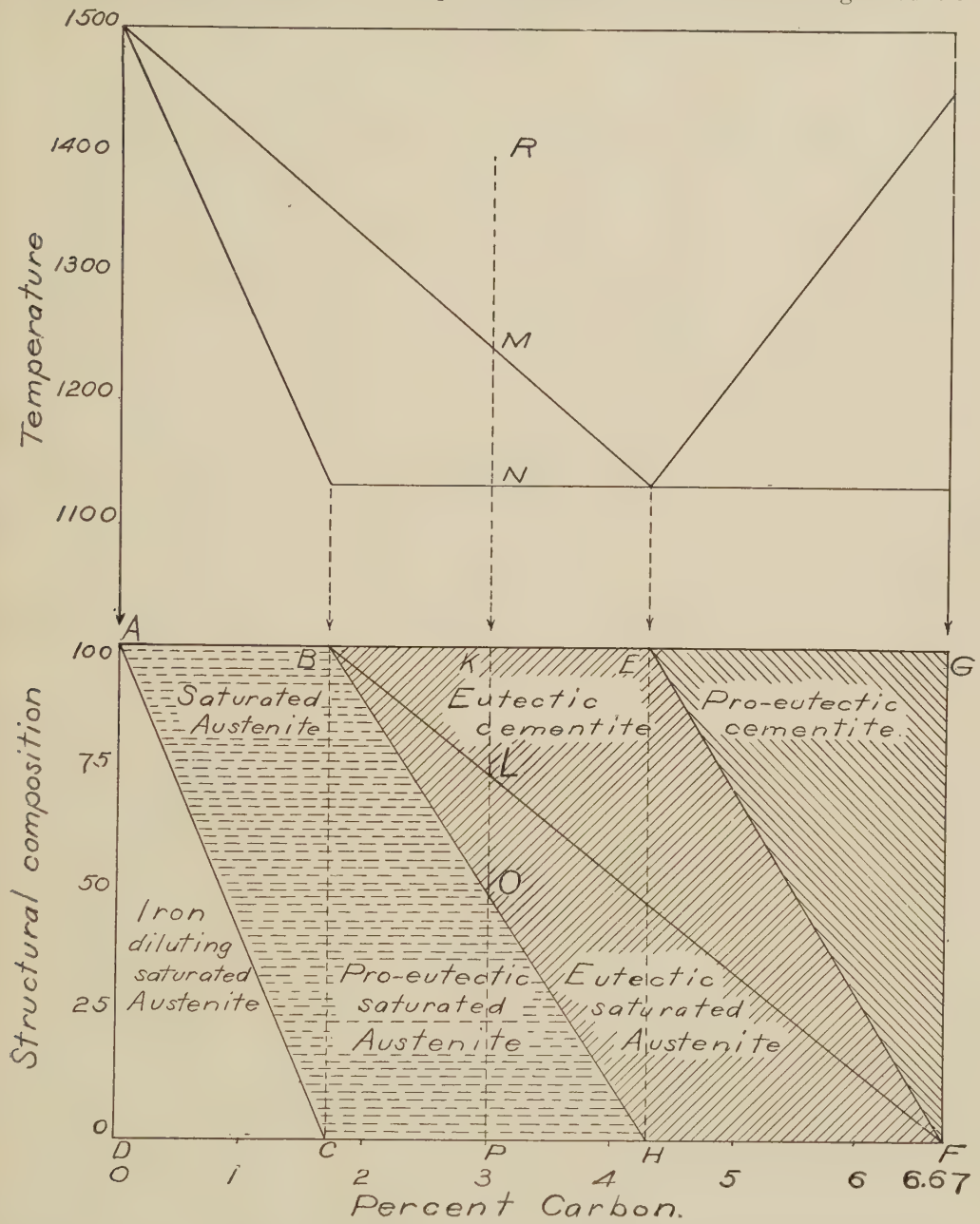


Fig. 387. — Fusibility curve and structural composition diagram of iron-carbon alloys.

free cementite, and a decreasing amount of eutectic, the latter disappearing altogether when the metal contains 6.67per cent carbon.[1]

[1] Howe questions the existence below solidification of pro-eutectic cementite on the ground that it graphitizes as soon as formed unless the cooling be extremely rapid or considerable manganese be present.

A modified form of the structural composition diagram may profitably be combined with the equilibrium diagram, as shown in Figure 387. Its interpretation should be obvious. The area *ABCD* represents the structural composition of all alloys containing less than 1.70 per cent of carbon, and shows that they are made up of 100 per cent of austenite. By dividing this area by the line *AC*, however, it is further shown graphically that the composition of the austenite of these alloys varies, and that they may be considered as being made up of *ABC* saturated austenite *diluted* by *ADC* pure iron, clearly indicating that with 0 carbon the alloy is entirely made up of iron and with 1.70 per cent carbon entirely of saturated austenite. The area *BCH* represents the proportion of free (pro-eutectic) saturated austenite formed during the solidification of any alloy containing between 1.70 and 4.3 per cent carbon. The area *BEFH* represents the proportion of eutectic present in any alloy containing more than 1.70 per cent of carbon. By dividing this area into two portions, moreover, by means of the line *BF*, we show graphically the relative proportions of saturated austenite and of cementite in the eutectic. Finally, the area *EGF* indicates the percentage of pro-eutectic cementite in any alloy containing more than 4.3 per cent carbon. To clarify, let us consider the alloy of composition *R* (3 per cent carbon). As it cools from *M* to *N* an amount of saturated austenite crystallizes, represented in percentage by the line *OP* of the structural composition diagram. At *N* an amount of eutectic alloy is formed, represented by the distance *KO*, made up of *KL* per cent of cementite and *LO* per cent of saturated austenite.

The percentage of cementite and of saturated austenite in the eutectic may be readily calculated by solving the equations

$$(1)\quad \mathrm{A} + \mathrm{Cm} = 100$$

$$(2)\quad \frac{1.70}{100}\mathrm{A} + \frac{6.67}{100}\mathrm{Cm.} = 4.30$$

in which A represents the percentage of austenite and Cm the percentage of cementite in the eutectic alloy, and which express the facts that the carbon present in the eutectic (4.3 per cent) is divided between the austenite and the cementite, the former containing 1.70 per cent carbon, the latter 6.67 per cent. The resolution of these equations shows that the eutectic alloy contains nearly 47.7 per cent of saturated austenite and 52.3 per cent of cementite. The structural composition of any iron-carbon alloy *immediately* after its solidification may likewise be readily calculated. If it contains less than 1.70 per cent carbon it is entirely made up of austenite. If more highly carburized, two cases are to be considered: (1) the alloy contains between 1.70 and 4.3 per cent carbon when it is made up of saturated austenite (A) and of eutectic (E) and (2) the alloy contains between 4.3 per cent and 6.67 per cent carbon when it is composed of cementite (Cm) and of eutectic (E).

In the first instance the two following equations

$$(1)\quad \mathrm{A} + \mathrm{E} = 100$$

$$(2)\quad \frac{1.70}{100}\mathrm{A} + \frac{4.3}{100}\mathrm{E} = \mathrm{C}$$

will give the values of A and E for any known carbon content (C), while in the latter case the equations

$$(1)\quad \mathrm{Cm} + \mathrm{E} = 100$$

$$(2)\quad \frac{6.67}{100}\,\mathrm{Cm} + \frac{4.3}{100}\,\mathrm{E} = \mathrm{C}$$

will likewise give the values of Cm and E.

An alloy, for instance, containing 3 per cent of carbon will be found to contain 50 per cent of eutectic and 50 per cent of saturated austenite, while an alloy with 5 per cent carbon is composed of 70.5 per cent of eutectic and 29.5 per cent free cementite.

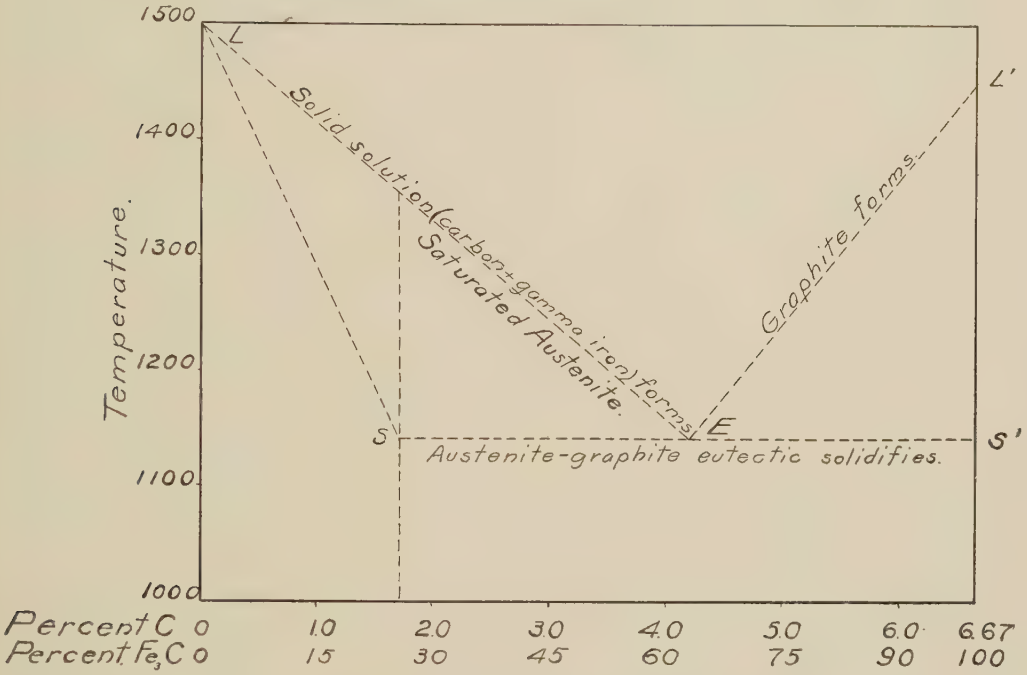


Fig. 388. — Iron-graphite fusibility curve of iron-carbon alloys.

Iron-Graphite Fusibility Curve. — It has already been mentioned that some writers claim that graphite instead of cementite may, and if time be given does, form on solidification; in other words, that the eutectic alloy may be composed of saturated austenite and graphite, and that free graphite may separate during the solidification of alloys containing more than 4.3 per cent carbon. The diagram interpreting this assumption, which may be called the iron-graphite fusibility curve, is shown in Figure 388. It will be seen to be similar to the iron-cementite diagram (Fig. 385).

Combined Graphite-Cementite Diagram. — Recognizing the possibility of the formation of a graphite-austenite eutectic and of a cementite-austenite eutectic according to the rate of cooling, some writers, notably Charpy and Grenet, Heyn, and Benedicks, recommend the use of double solidification curves in the equilibrium diagram of iron-carbon alloys. These double curves are shown in Figure 389, the dotted lines referring to the austenite-graphite system. It will be noted that free graphite and the graphite-austenite eutectic form respectively at temperatures slightly higher than those at which free cementite and the cementite-austenite eutectic form, the solidification of the latter constituents being regarded as due to surfusion or undercooling. It is accordingly believed that only the iron-graphite system is stable, the

iron-cementite system being "metastable." Our reasons for believing that graphite and not cementite is the final condition to be assumed by carbon are based on repeated and concordant observations that any condition promoting stable equilibrium results in the transformation of cementite into graphite, as, for instance, very slow cooling during and below solidification or long exposure of cementite (as in the manufacture of malleable cast-iron castings) to a high temperature, while on the contrary, treatments opposing equilibrium, such as quick cooling, always result in the formation or retention of cementite. Roozeboom, when he first took up the study of the iron-carbon diagram, believed that cementite was the final stable condition of carbon, any

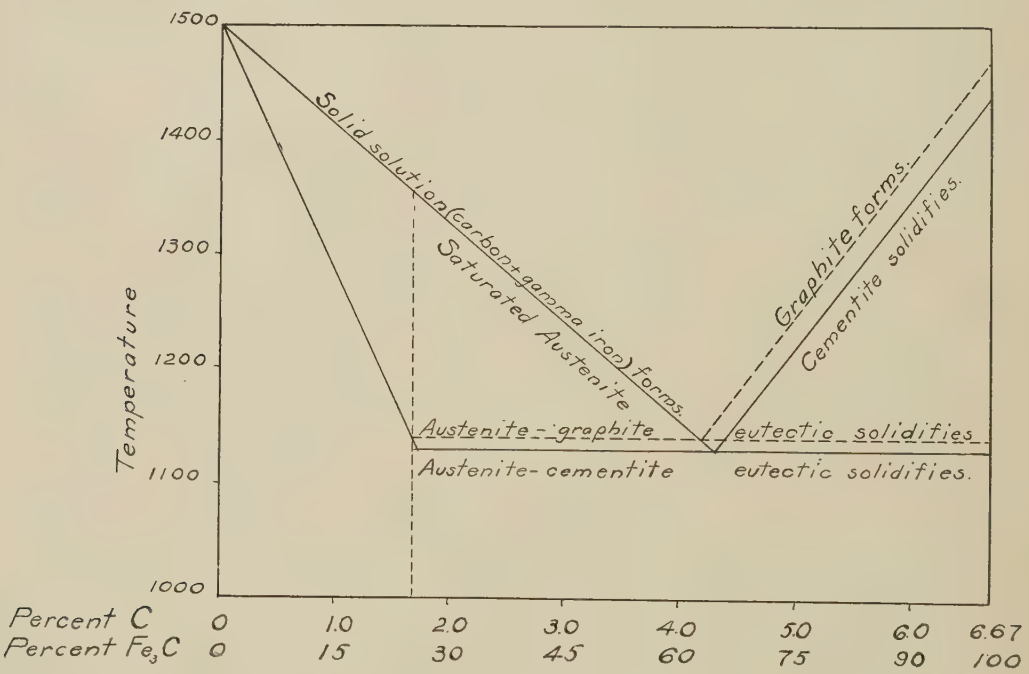


Fig. 389. — Combined graphite-cementite fusibility curves of iron-carbon alloys.

graphite having formed during solidification combining with iron at some 1000 degrees C. to form cementite. The error of this view soon became apparent, however, to Roozeboom himself.

Graphitizing of Cementite. — Although recognizing the fact that graphite and not cementite must be the final condition assumed by carbon, the author believes with some other observers that graphite never forms directly as iron-carbon alloys solidify, its occurrence always resulting from the breaking up of cementite according to the reaction

$$Fe_3C = 3\,Fe + C$$

from which it would follow that the iron-graphite fusibility curve need not be included in the equilibrium diagram. Even those who believe in the possibility of the direct formation of graphite do not deny that cementite is the constituent which generally forms first on solidification; they state that the separation of graphite from molten iron is possible only in the case of very slow cooling. As a matter of fact, however, they offer no conclusive evidences that such separation ever takes place. From

the formation of "kish," that is, of graphite floating on the surface of a ladleful of molten cast iron, it does not follow that such graphite formation was not preceded by the formation of cementite. If, on very slow cooling, graphite separated directly from molten iron, the bulk of it at least should rise to the top of the molten bath and the solidified mass should be found *much* richer in graphite near its surface than at some distance from it. The author does not understand such heterogeneity in the distribution of graphitic carbon to be observed in the case of gray cast-iron castings.[1] On the contrary, on the assumption that graphite results from the breaking up of cementite soon after its solidification, it is readily understood why, in spite of their very great difference in specific gravity, iron and graphite are found uniformly distributed in the various parts of castings. The microscopical examination of the structure of very slowly cooled castings does not reveal the existence of a graphite-austenite eutectic.

That cementite is unstable, being readily converted into iron and graphitic carbon, is also generally admitted. It is upon this instability of cementite that the important industrial operation of converting white cast-iron castings into graphitic malleable castings is based. And there is abundant evidence that the higher the temperature, the more readily is cementite dissociated, from which it follows that the higher the temperature at which cementite *forms* the more readily will it be converted into graphitic carbon. Bearing this in mind, and with the assistance of the diagram of Figure 387, let us look more closely into the graphitizing of cementite. The diagram shows clearly that, during the solidification of alloys containing more than 1.70 per cent of carbon, (1) some cementite forms as pro-eutectic cementite if the metal contains more than 4.3 per cent carbon, (2) some cementite forms as eutectic cementite in all alloys, (3) some cementite remains dissolved in the eutectic-austenite of all alloys, and (4) some cementite remains dissolved in the free austenite of alloys containing less than 4.3 per cent carbon. Considering first the free cementite, that is, the pro-eutectic and the eutectic cementite, it is evident that the former is formed at a higher temperature, and that the more carbon in the alloy the higher the temperature at which it begins to form. It seems safe to infer, therefore, that pro-eutectic cementite will break up into graphite and ferrite more readily than eutectic cementite, this being consistent with the well-known fact that hyper-eutectic alloys are generally rich in graphite even after relatively quick cooling. The presence of pro-eutectic cementite may also promote the formation of graphitic carbon because once this graphitizing process is started, it is likely to extend, if time be given, to the bulk of the cementite, first the eutectic cementite and later the austenite-cementite undergoing the change. Alloys containing less than 4.3 per cent carbon and consequently free from pro-eutectic cementite should not become graphitic so readily because of the lower temperature at which eutectic-cementite forms. If a large proportion of cementite be formed, however, that is, if the alloys contain more than 3 or 3.5 per cent of carbon, a certain amount of graphitizing is readily induced through slow cooling. With decreasing carbon the breaking up of cementite becomes progressively more difficult until, in alloys containing less than 1.70 per cent carbon (the steel series), and therefore free from eutectic cementite, graphitic carbon is very seldom formed.

[1] Howe reports the segregation of graphite in the upper part of kish-bearing cast iron, but this is readily explained on the ground that such irons must be hyper-eutectic in composition and that the pro-eutectic cementite beginning to graphitize while the iron is still partially liquid shows a tendency to rise to the top, hence indeed the formation of kish.

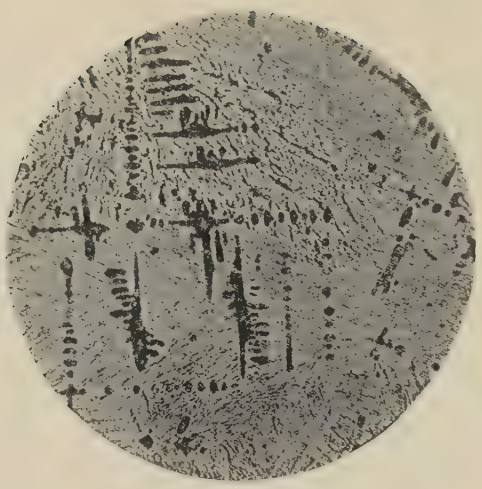


Fig 390. — Magnified 50 diameters.

Fig. 391. — Magnified 750 diameters.

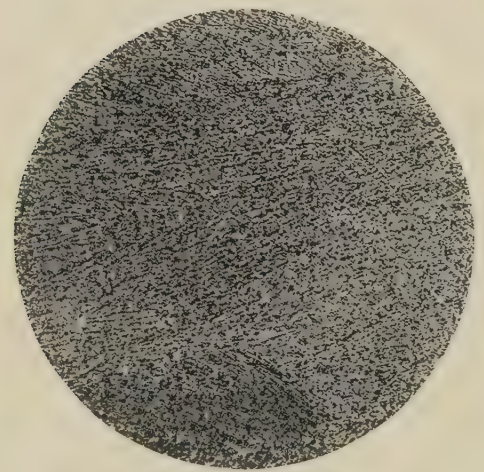


Fig. 392. — Magnified 50 diameters.

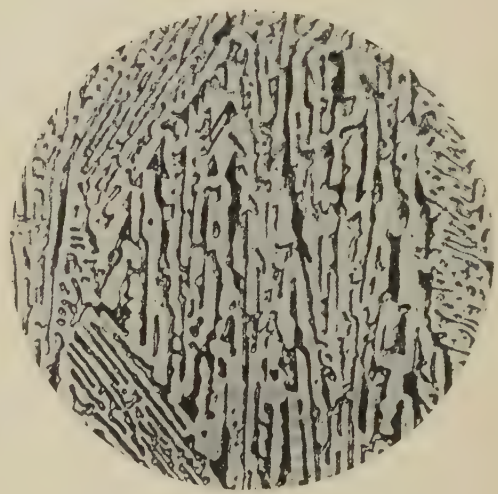


Fig. 393. — Magnified 750 diameters.

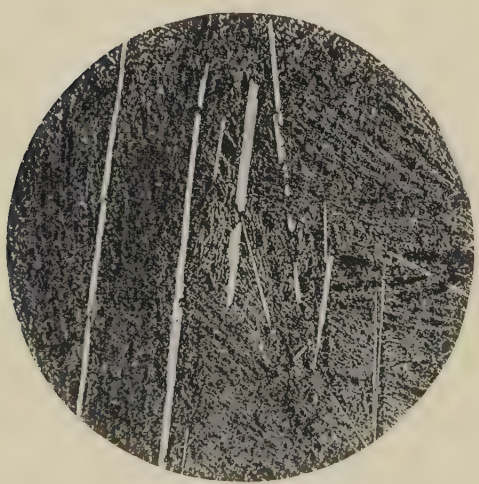


Fig. 394. — Magnified 50 diameters.

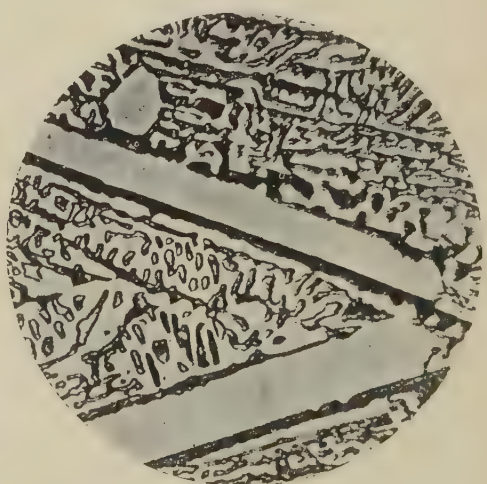


Fig. 395. — Magnified 750 diameters.

Figs. 390 and 391. — Iron-carbon alloy. Hypo-eutectic. Structure immediately after solidification. Dark crystallites of saturated austenite in a matrix of austenite-cementite eutectic. Figs. 392 and 393. — Iron-carbon alloy. Austenite-cementite eutectic. Figs. 394 and 395. — Iron-carbon alloy. Hyper-eutectic. Structure immediately after solidification. Needles of cementite in a matrix of austenite-cementite eutectic. (Gœrens.)

It should be borne in mind that while those alloys which contain but a small proportion of carbon cannot be made graphitic, when a large proportion of carbon is present the graphitizing once started may be made to include the totality of the cementite, thus explaining the freedom of steel from graphite and the freedom of some cast irons from cementite.

The foregoing remarks apply to pure iron-carbon alloys, the influence of the elements generally present in commercial products having been purposely ignored. When dealing with commercial steel and cast iron, the well-known influence of silicon in promoting the formation of graphitic carbon should be remembered as well as the opposite influence of sulphur and manganese. Because of the presence of a notable proportion of silicon, commercial cast irons after slow cooling are necessarily more graphitic than pure alloys of same carbon content.

Structure of Iron-Carbon Alloys Immediately after Solidification. — If the alloy contains less than some 1.70 per cent carbon it is made up after complete solidification of crystalline grains of austenite. It has been explained, however, that in the absence of manganese or other "retarding" elements it is not possible to prevent, even through very rapid cooling, the transformation of some of the austenite, at least, into martensite. The polyhedral structure of austenite has been illustrated in these pages in the case of special steels (manganese and nickel steels) and it is now well understood that the frequent network structures of slowly cooled steel are due to the existence of polyhedral austenitic structures above their critical range.

If the alloy contains from 1.70 to 4.3 per cent carbon it is made up, after solidification, of crystals of saturated austenite and of eutectic alloy. This is well shown after Gœrens in Figure 390, in which the dark "pine tree" crystals consist of saturated austenite, while the ground mass is the cementite-austenite eutectic.[1] In Figure 391 the same structure is shown more highly magnified. If the alloy contains exactly 4.3 per cent carbon, it consists wholly of eutectic, as shown under different magnifications in Figures 392 and 393. It has been seen that, theoretically, this eutectic contains 47.7 per cent of saturated austenite (the dark constituent), and 52.3 per cent of cementite. Alloys containing more than 4.3 per cent carbon consist after solidification of free cementite in the form of needles embedded in a eutectic matrix, as shown in Figures 394 and 395.

It should be noted that the dark constituent occurring in these structures and described as saturated austenite may not be absolutely unaltered austenite because of the difficulty of completely preventing the transformation of that constituent even in the presence of a large amount of carbon and by very sudden cooling. If the austenite has undergone some transformation, however, so that it contains some martensite and even troostite, those transformations must have taken place *in situ* and the structures reproduced in Figures 390 to 395 must represent accurately the structural aspect of the corresponding alloys after solidification.

Complete Equilibrium Diagram. — In the foregoing pages only the solidification curves of iron-carbon alloys have been considered and the probable mechanism of their freezing explained. Their equilibrium diagram, however, must include all heat evolutions observed on cooling from the liquid condition to atmospheric temperature; in other words, the thermal critical points fully described in previous chapters are part of the complete equilibrium diagram as indicated in Figure 396.

[1] Wüst has suggested the name of "ledeburite" for this eutectic in honor of the late well-known German metallurgist, A. Ledebur.

Since the meaning of every curve of this diagram has been discussed, it only remains to inquire into any possible structural or other changes taking place *after* solidification and *before* the alloys reach their respective thermal critical point or points, that is, while they cool from the solidus LSS' to the eutectoid line CDF. The changes which do or may take place as the alloys cool in this range are clearly stated in Figure 397. In this diagram the most likely significance of every curve is indicated

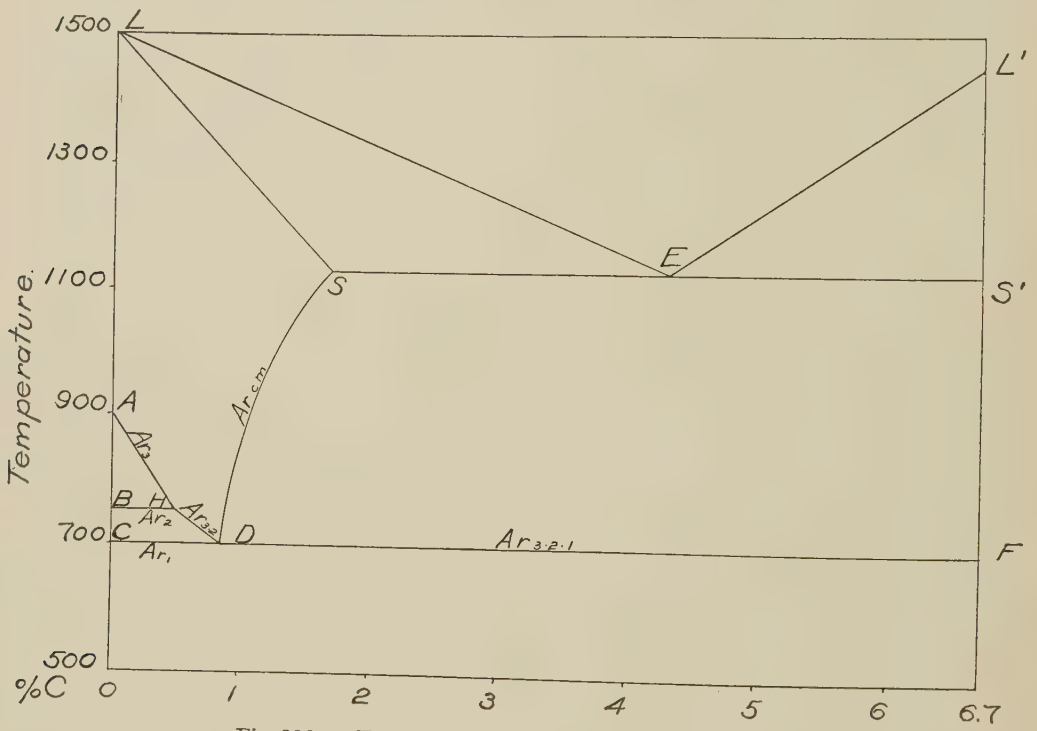


Fig. 396. — Equilibrium diagram of iron-carbon alloys.

as well as the nature of all structural transformations, and of all possible resulting structures after complete cooling. The author believes that it embodies those inferences best supported by analogy and by experimental evidences. Although necessarily involving some repetition, a methodical examination of the various parts of this complete diagram seems advisable, as it will permit a recapitulation of the various matters previously discussed.

Let us consider (1) the solidification of iron-carbon alloys, (2) their cooling from the solidus $LSES'$ to the eutectoid temperature CDF, and (3) their cooling through the eutectoid temperature and their final structures.

According to the mechanism of their solidification, iron-carbon alloys are divided into three classes, namely, (1) alloys containing less than 1.70 per cent of carbon, (2) alloys containing between 1.70 and 4.3 per cent carbon, and (3) alloys containing more than 4.3 per cent of carbon. Alloys containing less than 1.70 per cent of carbon, and including therefore all the steels of commerce, solidify as solid solutions of the carbide Fe_3C (cementite) in gamma iron, these solutions being known as austenite.[1]

[1] The possible formation of delta iron when alloys containing less than 0.38 per cent carbon solidify, followed by the transformation of delta into gamma iron, will soon be considered.

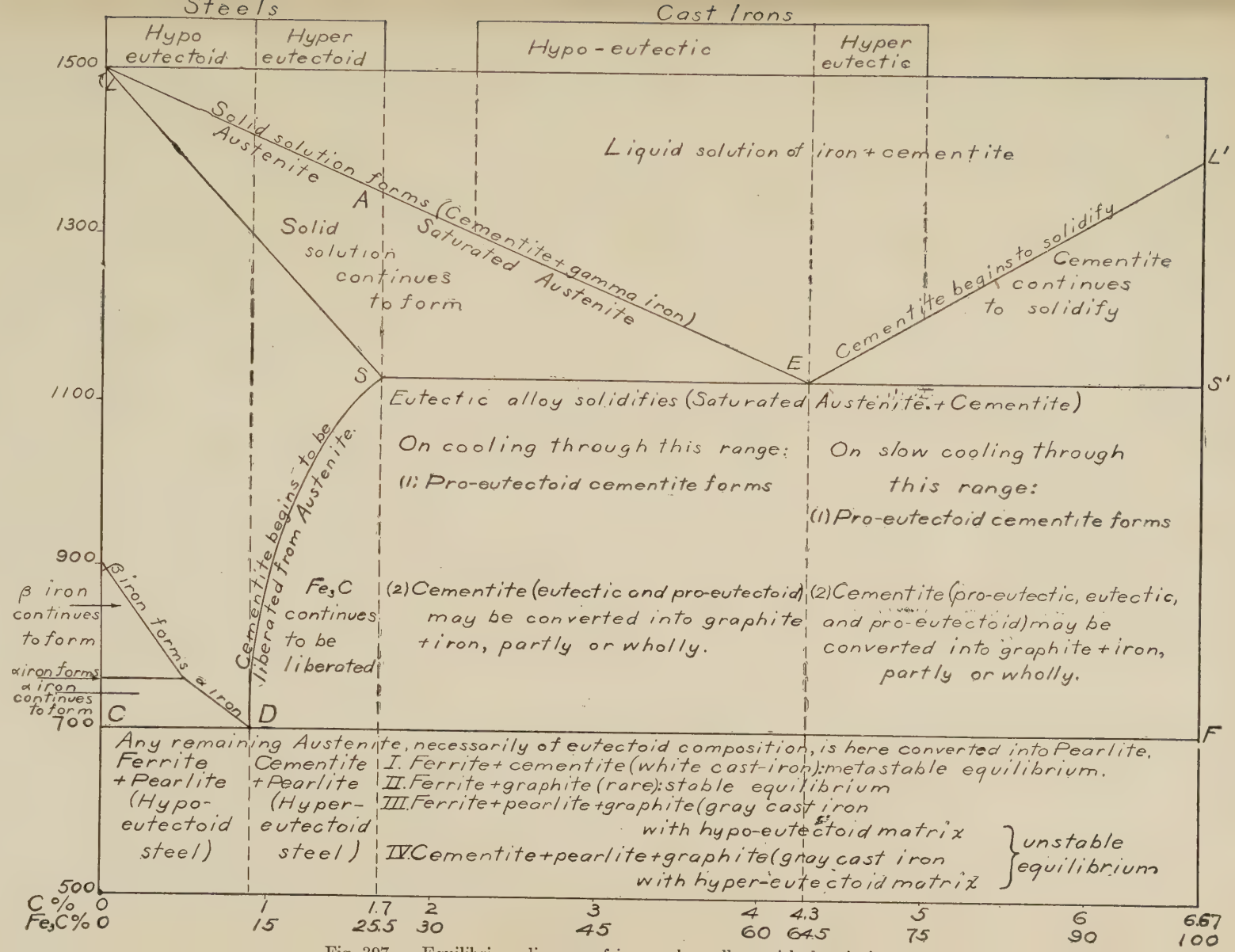

Steels
Cast Irons
Hypo eutectoid
Hyper eutectoid
Hypo-eutectic
Hyper eutectic
1500
1300
1100
900
700
500
L
L'
S
S'
E
F
A
C
D
Solid solution forms (Cementite + gamma iron) Saturated Austenite
Liquid solution of iron + cementite
Solid solution continues to form
Cementite begins to solidify
Cementite continues to solidify
Eutectic alloy solidifies (Saturated Austenite + Cementite)
On cooling through this range:
(1) Pro-eutectoid cementite forms
On slow cooling through this range:
(1) Pro-eutectoid cementite forms
Cementite begins to be liberated from Austenite
Fe3C continues to be liberated
β iron continues to form
β iron forms α iron
α iron forms
α iron continues to form
(2) Cementite (eutectic and pro-eutectoid) may be converted into graphite + iron, partly or wholly.
(2) Cementite (pro-eutectic, eutectic, and pro-eutectoid) may be converted into graphite + iron, partly or wholly.
Any remaining Austenite, necessarily of eutectoid composition, is here converted into Pearlite.
Ferrite + Pearlite (Hypo-eutectoid steel)
Cementite + Pearlite (Hyper-eutectoid steel)
I. Ferrite + cementite (white cast-iron): metastable equilibrium.
II. Ferrite + graphite (rare): stable equilibrium
III. Ferrite + pearlite + graphite (gray cast iron with hypo-eutectoid matrix
IV. Cementite + pearlite + graphite (gray cast iron with hyper-eutectoid matrix
unstable equilibrium
C% 0 1 1.7 2 3 4 4.3 5 6 6.67
Fe3C% 0 1.5 2.5.5 3.0 4.5 6.0 6.4.5 7.5 9.0 10.0

Fig. 307. — Equilibrium diagram of iron and carbon alloys (Hoyt).

LA is the liquidus and *LS* the solidus of these alloys. Alloys containing between 1.70 and 4.3 per cent of carbon solidify through the formation of crystals of saturated austenite at gradually decreasing temperatures, and through the final solidification, at the eutectic temperature, of the residual molten metal, necessarily of eutectic composition. Alloys containing more than 4.3 per cent of carbon solidify through the formation of cementite crystals at gradually decreasing temperatures, and through the final solidification, at the eutectic temperature, of the residual molten metal necessarily of eutectic composition.

In cooling below their solidus, *LS*, alloys with less than 1.70 per cent carbon undergo no change until they reach their thermal critical points Ar_3, $Ar_{3\cdot2}$, $Ar_{3\cdot2\cdot1}$, or Ar_{cm} as the case may be, when, if they contain less than some 0.85 per cent of carbon (hypo-eutectoid steels), some iron is set free and converted into beta iron (or alpha iron), while if they contain more carbon (hyper-eutectoid steels), cementite is liberated. In either case when the eutectoid temperature is reached the residual austenite, now of eutectoid composition (0.85 per cent carbon), is converted into pearlite.

After solidification, alloys containing between 1.70 and 4.3 per cent carbon are aggregates of saturated austenite (austenite containing 1.70 per cent C or 25.1 per cent cementite) and of cementite-austenite eutectic. On cooling below their solidus, cementite (pro-eutectoid cementite) is liberated both from the free and from the eutectic-austenite, while if the cooling be sufficiently slow both the eutectic and pro-eutectoid cementite may be partly or wholly dissociated into graphite and iron (ferrite). Indeed, the graphitizing may even include the eutectoid cementite, in which case the alloy is made up solely of ferrite and graphite.

Alloys containing more than 4.3 per cent of carbon are, immediately after solidification, aggregates of cementite (pro-eutectic cementite) and of cementite-austenite eutectic. On slow cooling below their solidus, cementite (pro-eutectoid cementite) is liberated from the eutectic austenite, while the pro-eutectic, eutectic, and pro-eutectoid cementite may be partly or wholly dissociated into graphite and ferrite, in some extreme cases the eutectoid cementite even being graphitized.

On cooling through the eutectoid temperature, any remaining austenite is bodily converted into pearlite.

The above consideration clearly shows that in alloys containing more than some 1.70 per cent carbon four types of structure may be formed according to the rate of cooling below the solidus:

(I) Cementite plus pearlite, the structure of white cast iron, readily produced by quick cooling and representing a metastable equilibrium. (II) Ferrite and graphite, an extreme case, possible only after very slow cooling and in the presence of much silicon, little manganese, and sulphur, and representing stable equilibrium. (III) Cementite plus pearlite and graphite, the structure of gray cast iron with hyper-eutectoid matrix, resulting from slow cooling, promoted by the presence of silicon and opposed by sulphur and manganese. (IV) Pearlite, ferrite, and graphite, the structure of gray cast iron with hypo-eutectoid matrix, produced because of slower cooling or because of the presence of more silicon or of less sulphur and manganese.

It will be explained in the next chapter that, according to the phase rule, only two components may be present in a binary alloy in a state of equilibrium, from which it follows that gray cast irons, since they contain besides iron both cementite and graphite, are out of equilibrium. One of the components must disappear if the alloy is to assume equilibrium. Cementite is undoubtedly that component, as proven by

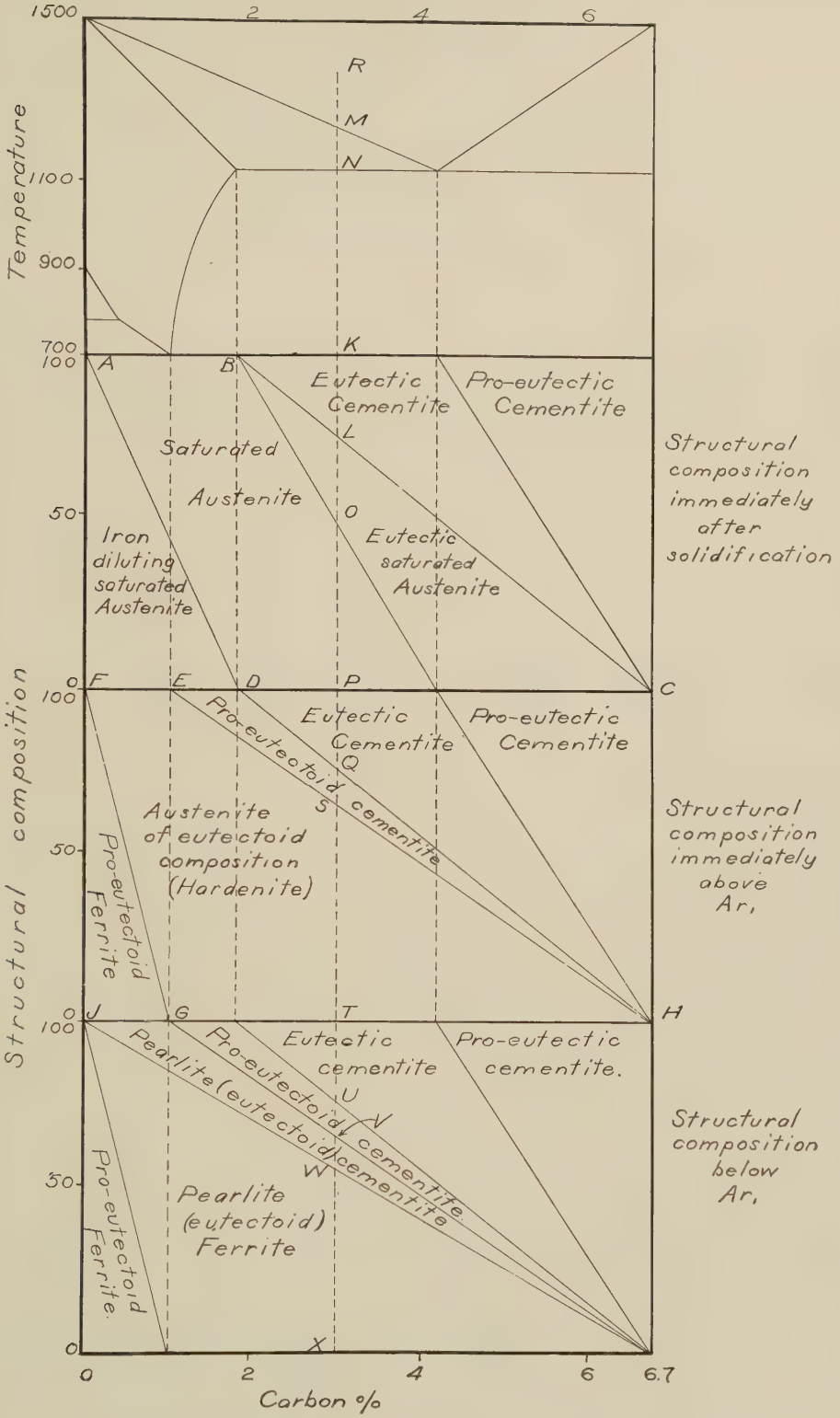


Fig. 398. — Equilibrium and structural composition diagram of iron-carbon alloys.

the malleablizing of cast iron, when cementite is readily dissociated into graphite and ferrite on prolonged heating to a high temperature.

In Figure 398 the complete equilibrium diagram is shown, combined with three constitutional diagrams showing graphically the structural composition of iron-carbon alloys (1) immediately after their solidification, (2) immediately before the eutectoid temperature, and (3) below the eutectoid temperature, *on the assumption that no graphitic carbon is formed.* The structural changes taking place while the alloys cool below their solidus down to the eutectoid temperature are, in this way, clearly

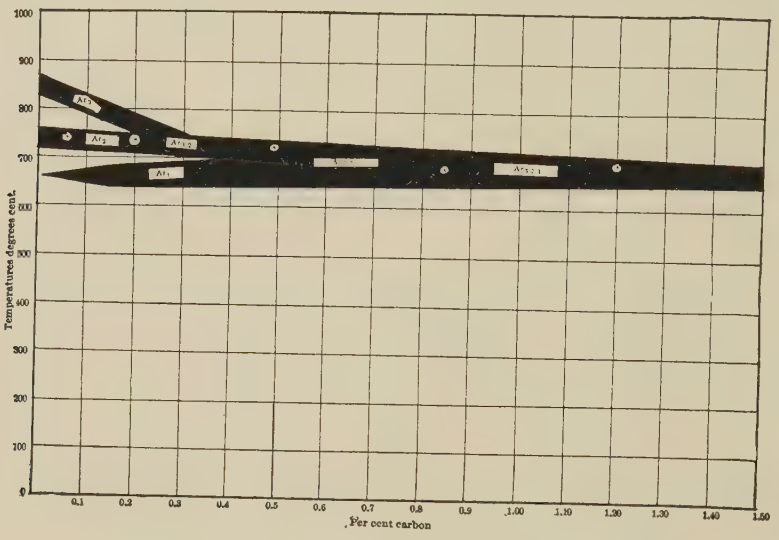


Fig. 399. — The author's early equilibrium diagram (1896).

depicted. The following facts, for instance, are graphically shown: (1) the pro-eutectic cementite formed during the solidification of hyper-eutectic alloys and the eutectic cementite present in all alloys containing more than 1.70 per cent carbon remain unchanged as the alloy cools to atmospheric temperature, (2) the free saturated austenite of hypo-eutectic alloys, as well as the eutectic-austenite, are converted into eutectoid austenite through the liberation of cementite (pro-eutectoid cementite), the area *EDH* representing the cementite thus set free, and (3) in hypo-eutectoid alloys iron is set free, as shown by the area *FJG*. The lower diagram shows that, in cooling through the eutectoid temperature, the remaining austenite, now necessarily of eutectoid composition, and sometimes called hardenite, is converted into pearlite. Taking, for instance, the metal whose composition and temperature are represented by the point *R*, its transformations and final structure are clearly shown. At *M* it begins to solidify through the formation of crystals of saturated austenite; from *M* to *N* the austenite crystals continue to grow, the percentage of free austenite present in the solidified metal being represented by the distance *OP*; at *N* the residual bath solidifies as a eutectic alloy, the percentage of which is proportional to the distance *KO*; this eutectic contains $KL = PQ = TU$ per cent of cementite and *LO* per cent of saturated austenite; *LP* is the total amount of austenite in the alloy; after solidification in cooling from *N* to *K*, pro-eutectoid cementite is liberated both from the free and from the eutectic austenite, *QS* representing the percentage of cementite finally expelled; on reaching the point *K*, the remaining austenite, *ST*, is of eutectoid

composition, when it is sometimes called hardenite, and in cooling through K this austenite is converted into pearlite, the metal being finally made up of TU per cent of eutectic cementite, UV per cent of pro-eutectoid cementite, and VX per cent of pearlite, the latter containing VW per cent of cementite, and WX per cent of ferrite, or of TV per cent of free cementite and VX per cent of pearlite, or again of TW per cent of total cementite and WX per cent of ferrite.

Historical. — In view of the scientific and practical importance of the equilibrium diagram of iron-carbon alloys, a brief historical sketch of its evolution should be of

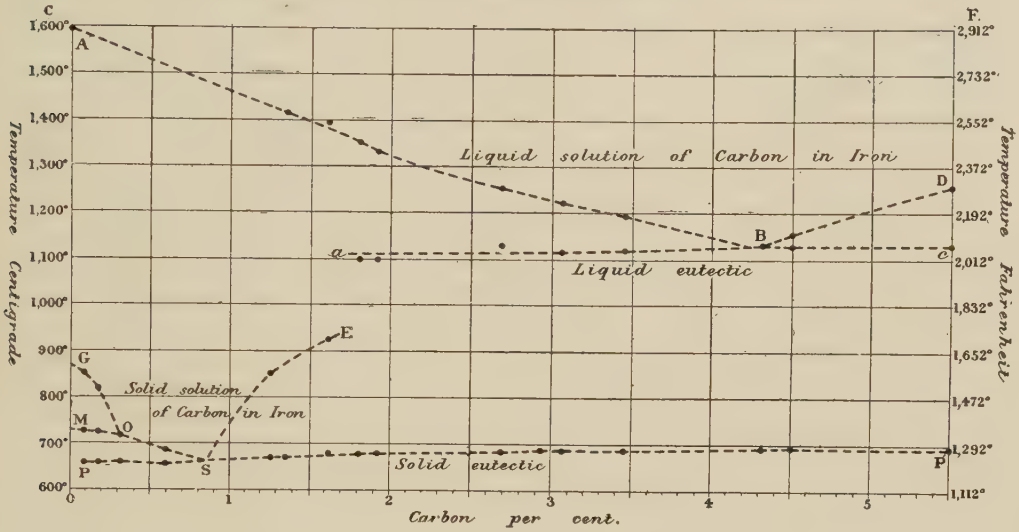


Fig. 400. — Roberts-Austen's first equilibrium diagram (1897).

interest to the reader. The first diagram was published by the author in 1896.[1] It is reproduced in Figure 399. It will be noted that, although the diagram includes only the thermal critical points, it is otherwise substantially accurate. In describing it the author wrote in part:

"Figure 1 shows graphically the position of the critical points in *cooling* steels of various carbons. The width of the black lines does not refer to the intensity of the retardations, but only indicates the range of temperature which they cover. For instance, it shows that the single retardation of high carbon steel begins at about 680 deg. C. and ends at about 640 deg. C. The maximum evolution of heat lies somewhere between these limits, but not necessarily in the middle.

"This graphical representation was obtained by plotting the results of the investigations of Osmond, Howe, Roberts-Austen, Arnold, and the writer; and, with one or two exceptions all their figures fall very nearly within the limits here indicated."

It is from this modest beginning that the present diagram was evolved.[2]

In 1897 Roberts-Austen published in his fourth report of the Alloys Research Committee of the Institution of Mechanical Engineers the diagram reproduced in Figure 400.

[1] "The Microstructure of Steel and the Current Theories of Hardening," Albert Sauveur, Transactions American Institute of Mining Engineers. 1896, p. 867.

[2] Since these remarks were written Prof. H. M. Howe has expressed the opinion that credit for the first equilibrium diagram is due to Reinhard Mannesmann.

Two years later, in 1899, the diagram shown in Figure 401 was published by Roberts-Austen and Stansfield in the fifth report of the Alloys Research Committee.

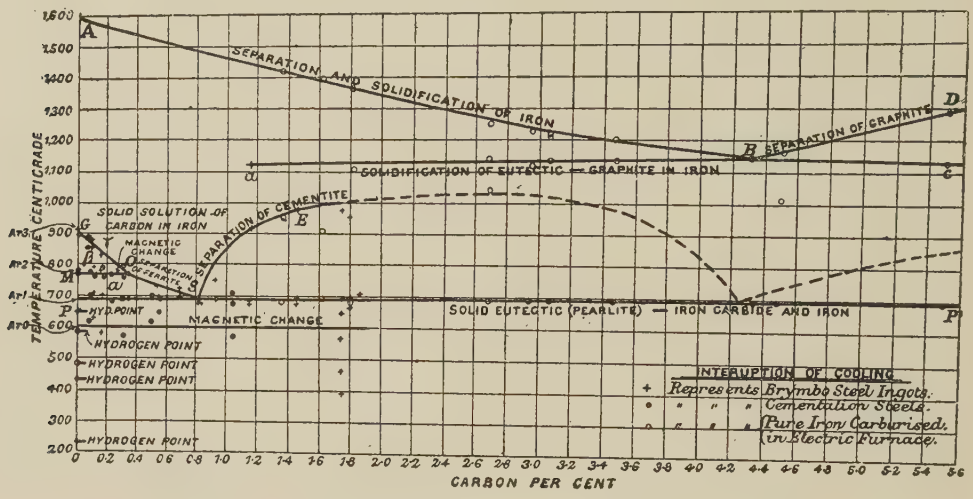


Fig. 401. — Roberts-Austen's second equilibrium diagram (1899).

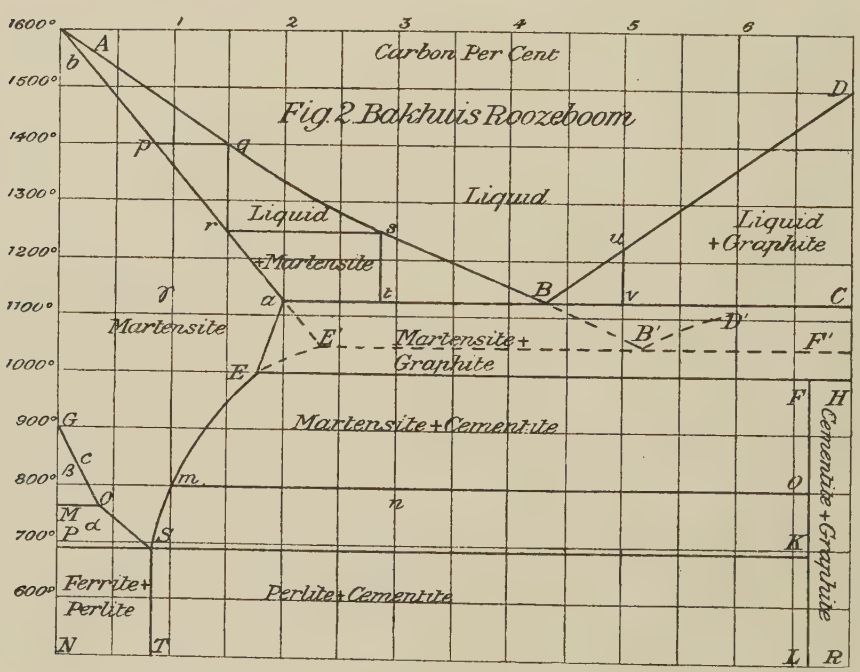


Fig. 402. — Roozeboom's equilibrium diagram (1900).

Some of the conspicuous features of this diagram should be noted. The solidification point of pure iron was indicated to be 1600 deg. C., whereas we know now that it is nearly 1530 deg. No attempt had been made yet at ascertaining the end of the solidification, that is the solidus, of alloys forming solid solutions; the formation of a eutectic on solidification was indicated as taking place in alloys containing more than one per cent carbon; graphite was supposed to crystallize during the solidification of alloys

containing more than 4.3 per cent carbon, there being in the diagram no indications of possible formation of cementite; the eutectic alloy was assumed to be a graphite-iron eutectic; critical points occurring below the eutectoid temperature were represented in the diagram and marked "hydrogen points," the Ar_{cm} curve was arbitrarily extended to yield a V-shaped curve. Roberts-Austen mentioned the formation of a solid solution, free in hypo-eutectic steels, and as a constituent of the eutectic in alloys of eutectic composition, and he ascribed the presence of free cementite in cast iron to the liberation of that constituent from solid solution.

In 1900 Roozeboom took up the study of Roberts-Austen's diagram, and applying to it the teachings of the phase rule published the diagram of Figure 402 as a probably accurate representation of the solidification mechanism of iron-carbon alloys and of the structural transformations taking place after solidification. In this diagram, the line *ba*, that is the solidus of alloys forming solid solutions, is for the first time indicated; the word martensite is used instead of austenite to denote the solid solution of iron and carbon; free graphite is assumed to form during the solidification of alloys containing more than 4.3 per cent carbon and the constituents of the eutectic alloy are supposed to be martensite (solid solution) and graphite. The Ar_{cm} curve of hyper-eutectoid steels is arbitrarily extended as a horizontal line starting from *E* (1.75 per cent carbon and 1000 deg. C.) and extending to the end of the diagram. Roozeboom argued that, while graphite formed on solidification in all alloys containing more than 2 per cent carbon, this graphite at 1000 deg. (line *EF*) recombined with iron to yield cementite so that, finally, alloys in equilibrium would contain only ferrite and cementite, thus conforming to the phase rule which forbids the presence of more than two components in binary alloys. It has since been conclusively shown that Roozeboom was in error, that while the ferrite-cementite system is in equilibrium according to the phase rule, it is in metastable equilibrium, the ferrite-graphite system being the only stable one. The hypothetical horizontal line *EF* is now consequently omitted from the equilibrium diagram, and the Ar_{cm} curve made to join the eutectic line at its origin (*a*).

In 1904 Carpenter and Keeling made a series of very careful experiments in order to ascertain the evolutions of heat taking place in cooling pure iron-carbon alloys from the liquid state to atmospheric temperature. By plotting their results, the equilibrium diagram reproduced in Figure 403 was obtained. The solidification of pure iron is shown to take place at 1500 deg. C. The curves are otherwise identical to those of Roozeboom, the horizontal line *EF* having been introduced. The faint evolutions of heat occurring in the vicinity of 600 deg. C. already discovered by Roberts-Austen and ascribed by him to the presence of hydrogen, were also observed by Carpenter and Keeling, as well as some faint evolutions in the vicinity of 775 deg., the meaning of which remains uncertain.

When it became apparent that graphite and not cementite must be the final stable form of carbon, several authorities argued that two equilibrium conditions could exist according to the rate of cooling during solidification, one of them stable, the other metastable, and that this should be indicated in the diagram. This view was presented notably by Charpy and Grenet, by Benedicks and by Heyn. The double diagram advocated by them is represented in Figure 404. The solidification of free cementite and of the cementite-austenite eutectic being assumed to be due to the well-known phenomenon of surfusion or undercooling, the corresponding curves are arbitrarily outlined at temperatures slightly lower than those pertaining to the formation of free

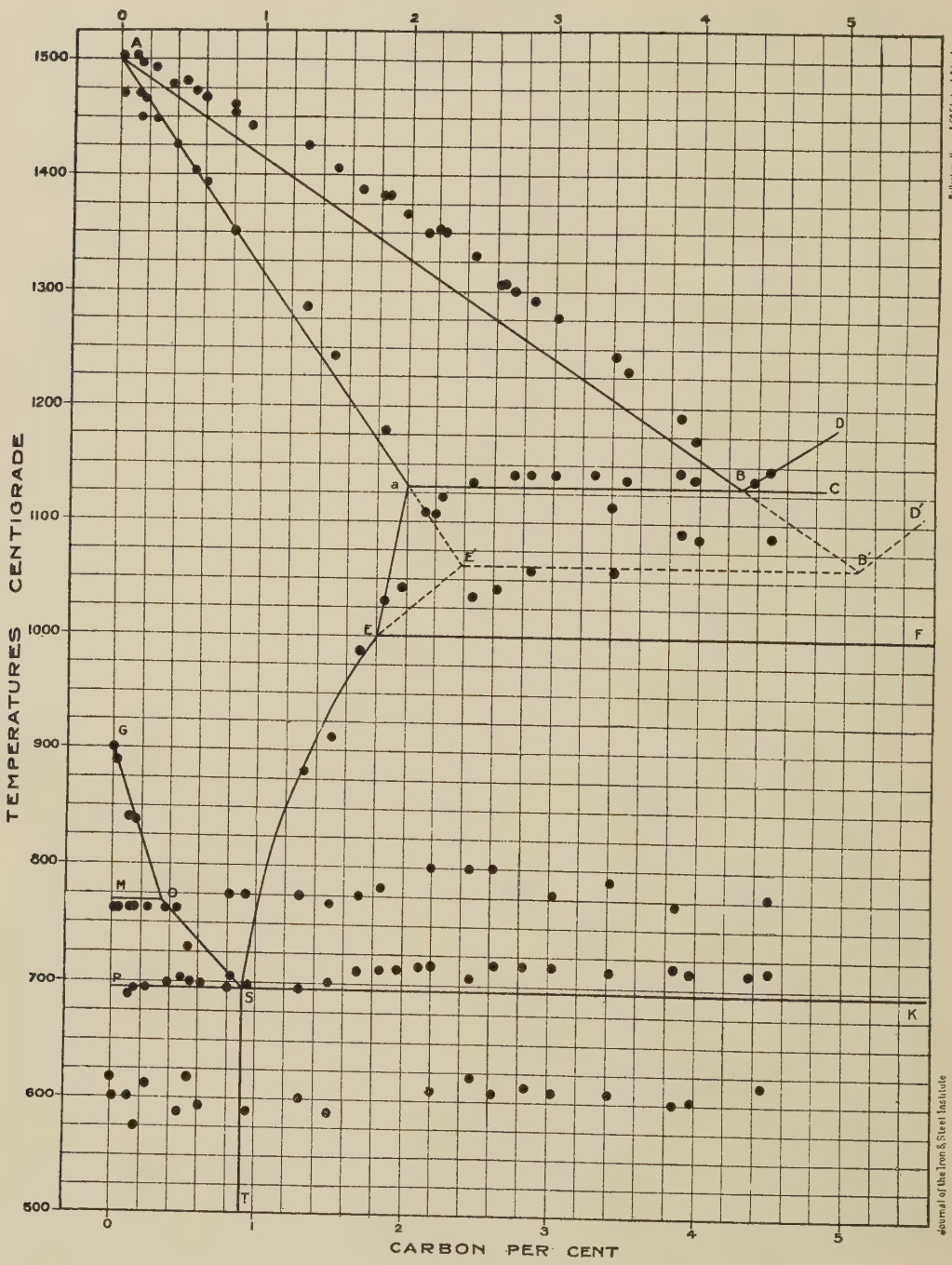


Fig. 403. — Carpenter's and Keeling's equilibrium diagram (1904).

graphite and of graphite-austenite eutectic. The author has already shown why, in his opinion, the graphite curves should be left out. The view that cementite always forms during the solidification of iron-carbon alloys but that being unstable it is

readily dissociated into ferrite and graphite, seems to be better supported by experimental evidences and more consistent with practical facts.

Rosenhain has recently plotted the experimental results of Carpenter and Keeling, of Gutowsky and of himself, obtaining the diagram reproduced in Figure 405. He considers Gutowsky's results in regard to the form of the solidus curve of alloys

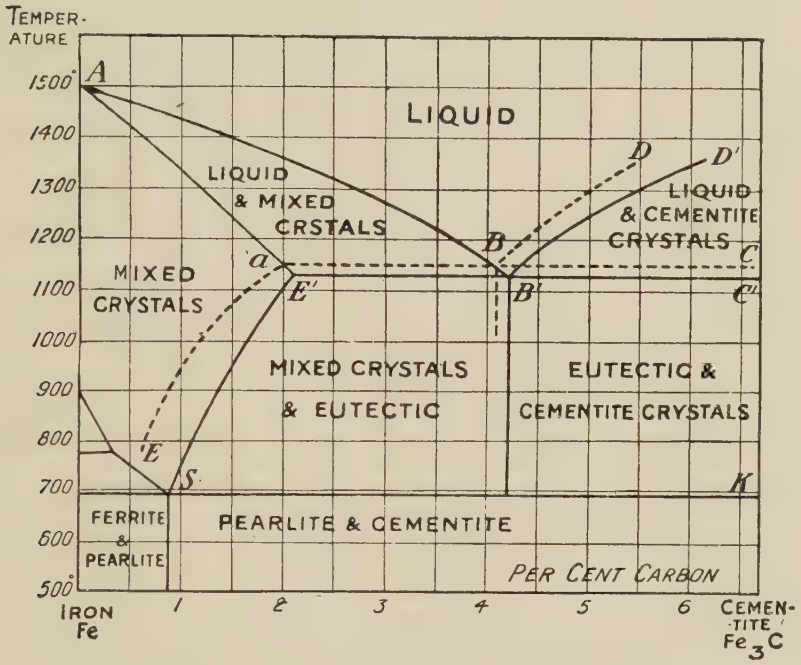


Fig. 404. — Benedicks' double equilibrium diagram.

forming solid solutions as more accurate than those previously published, and he incorporates them in the diagram as shown in Figure 405, the solidus line being rounded instead of straight, as heretofore represented. In justification of his course, Rosenhain writes:

"We have now to consider the curved portion of the 'solidus,' the line *AD*. This represents the temperatures at which the alloys have just completed their freezing process, that is, have just become completely solid, or, conversely, it represents the temperature of incipient fusion on heating. In the earlier investigations, and even in those of Messrs. Carpenter and Keeling, these temperatures were obtained by estimating the point on each of the cooling-curves where the heat-evolution due to solidification came to an end. Unfortunately, the *end* of a heat-evolution is never sharply indicated on the curves, so that this estimation was admittedly vague. Quite recently that determination has been repeated, and with considerably greater accuracy, because a very much more satisfactory method was available. . . .

"The method of determining the 'solidus' was to take small pieces of steel, of known composition, heat them, and suddenly cool them from successively higher temperatures; afterward each specimen was examined by means of the microscope. It is easy, as the photographs show, to determine what is the particular point at which you have reached a temperature where there was a small quantity of liquid metal present at the moment of quenching."

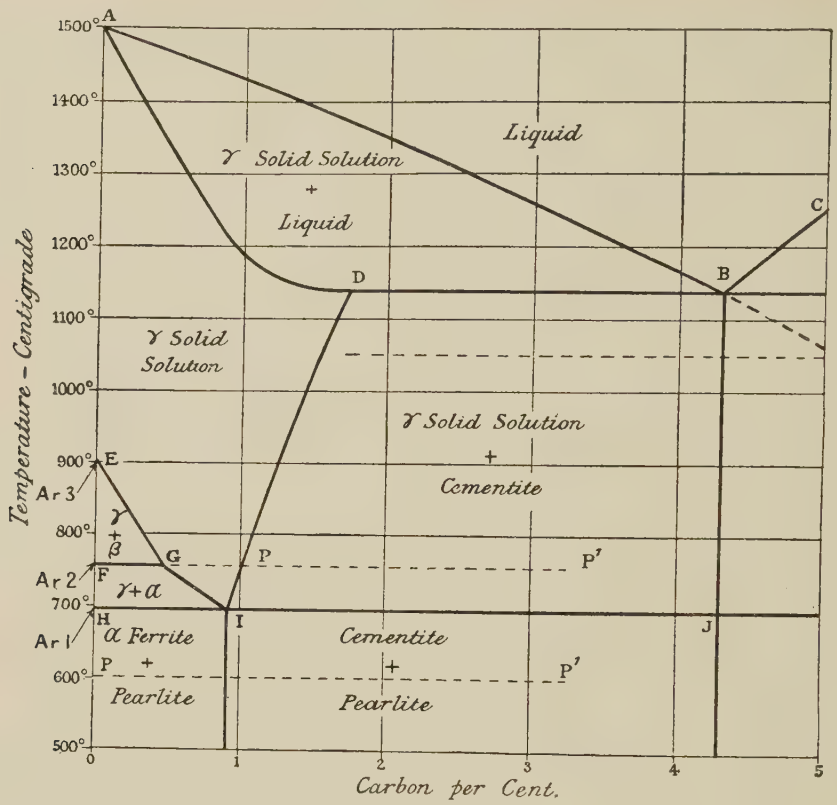


Fig. 405. — Rosenhain's equilibrium diagram (1911).

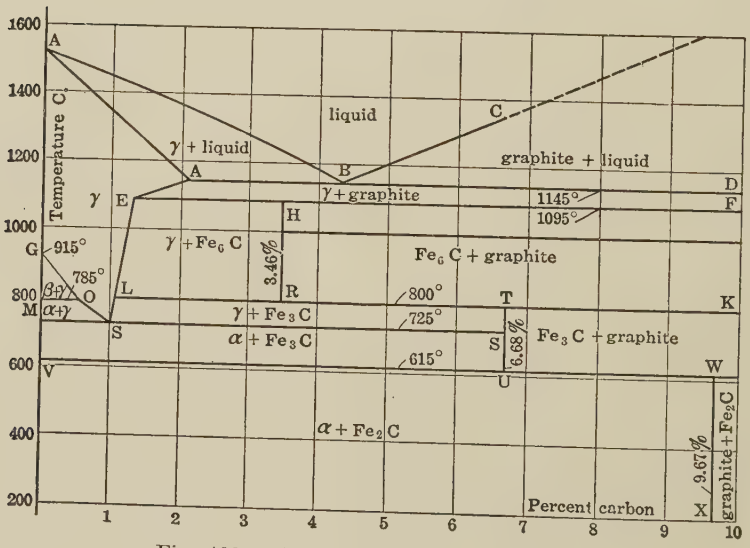


Fig. 406. — Upton's equilibrium diagram.

Upton's Diagram. — The rather revolutionary diagram shown in Figure 406 has been proposed by G. B. Upton. He considers it more satisfactory than the double diagram, as it does away with the necessary conception of a metastable and a stable

equilibrium at nearly the same temperature. Upton argues that cementite decomposes above 800 deg. C. into graphite and iron, but that even after prolonged annealing some 3.5 per cent carbon remains combined, from which it is inferred that the carbide Fe_6C forms (carbon 3.46 per cent) stable in the region *LEFK* in the diagram although he adds that it might be a solid solution containing that amount of

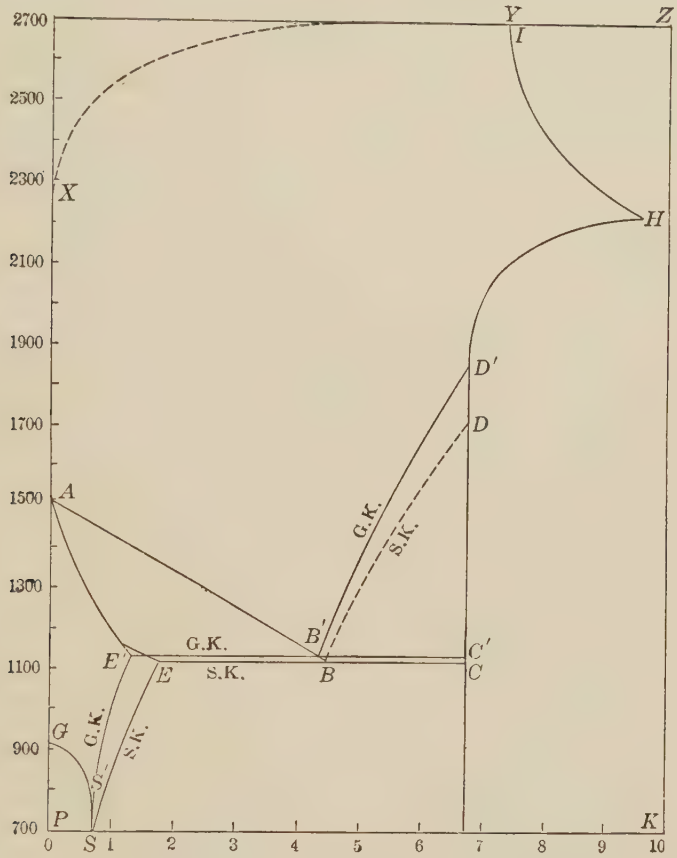


Fig. 407. — Ruff's equilibrium diagram.

carbon which forms at about 800 deg. Fe_6C is claimed to be converted into Fe_3C, thus accounting for the evolutions of heat in this region reported by Carpenter and Keeling. At about 600 deg., according to the diagram, Fe_3C is converted into Fe_2C, thus explaining the evolutions of heat detected at that temperature by many observers. It is very difficult to accept the hypothesis that graphite is not the stable condition of carbon in the area *LEHR* and that Fe_2C and not Fe_3C is the condition of the carbon remaining combined after complete slow cooling. The existence of both Fe_6C and Fe_2C is based on chemical tests the significance of which is far from evident. Justification for the line *EF* is claimed on the ground that evolutions of heat have been reported by Carpenter and Keeling as occurring at 1050 to 1100 deg. Other observers, however, have generally failed to detect these retardations. There are other serious objections to Upton's diagram and its construction is so highly speculative as to render its closer study inadvisable in these pages.

Ruff's Diagram. — Professor Ruff has published the equilibrium diagram reproduced in Figure 407, which, it will be noted, is of the double type, *GK* representing equilibrium with graphite and *SK* with cementite. The diagram does not extend below the eutectoid line *PK* but includes alloys containing as much as 10 per cent carbon. The line *D'H* indicates the increasing solubility of carbon in iron with in-

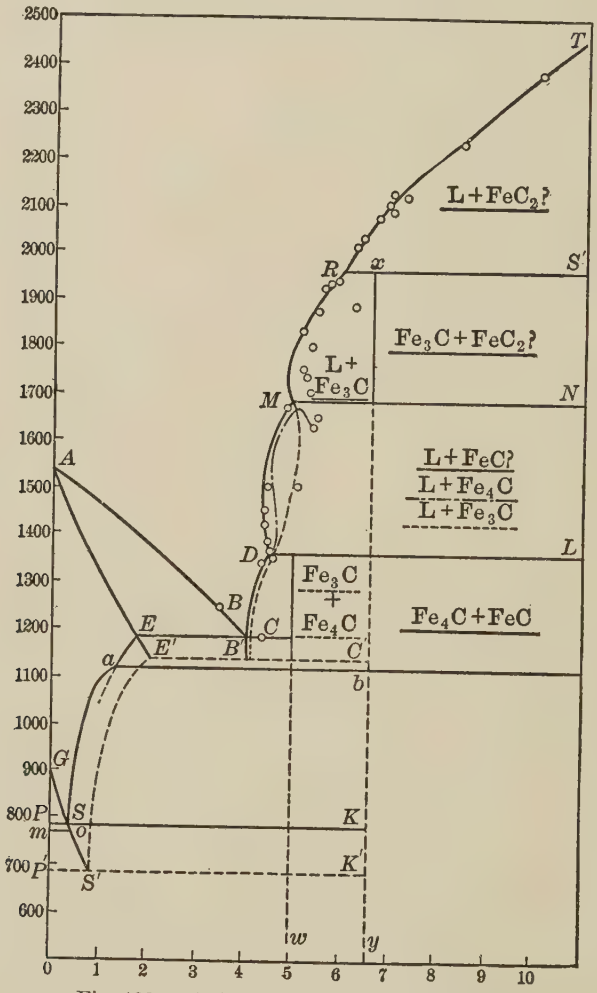


Fig. 408. — Wittorff's equilibrium diagram.

creasing temperature. At some 2200 deg. C. molten iron saturated with carbon contains nearly 10 per cent of that element. At this temperature Ruff believes that the alloy consists of the carbide Fe_2C, as explained in Chapter XXII. As the temperature increases above 2200 deg. the dissolving power of iron for carbon decreases, as indicated by the line *HI*, carbon being rejected, probably through the breaking up of some Fe_2C into iron and graphite (see Chapter XXII). At some 2700 deg. iron can retain but a little over 7 per cent of carbon in solution. In cooling below 2200 deg. (line *HD'*) graphite and Fe_3C are formed from the transformation of Fe_2C.

Wittorff's Diagram. — N. M. Wittorff worked out the diagram reproduced in Figure 408. It will be noted that (1) starting with an alloy containing some 11 per

cent carbon, as it cools from T to R, that is from some 2400 to 2000 deg. C., the carbide FeC_2 crystallizes out according to the diagram, (2) between R and M (2000 to 1700 deg.) Fe_3C forms through the transformation of some FeC_2, (3) between M and D (1700 to 1350 deg.) both FeC and Fe_4C are formed, necessarily at the expense of FeC_2, which disappears, and possibly also through the transformation of some of the Fe_3C, and (4) below D (1350 deg.) the liquid phase disappears.

Investigations of a region of the equilibrium diagram but little explored should be welcomed, but in view of the fact that the experimental results of the different observers as well as the conclusions based upon them are at such variance, it seems advisable to omit from these pages a closer scrutiny of these recent diagrams. When some of the points that need clearing up have been settled the matter involved will be duly incorporated in a subsequent edition of this treatise.

Honda's Recent Diagram. — In Figure 409 is shown a recent diagram after Honda which has been accepted by many as best representing our knowledge of the subject. It differs from the ordinary type (Fig. 397), which for many years has been used by metallurgists, (1) in the insertion of the A_4 point denoting the formation on solidification of delta iron in alloys containing less than 0.38 per cent carbon, (2) in including the A_0 point at 215 deg. C. in the form of a horizontal line, and (3) in indicating the occurrence of the A_2 point also as a horizontal line, Honda believing that it does not merge with the A_3 point. On the ground that A_2 and A_0 do not indicate changes of phases, the horizontal lines indicating their occurrence have been dotted.

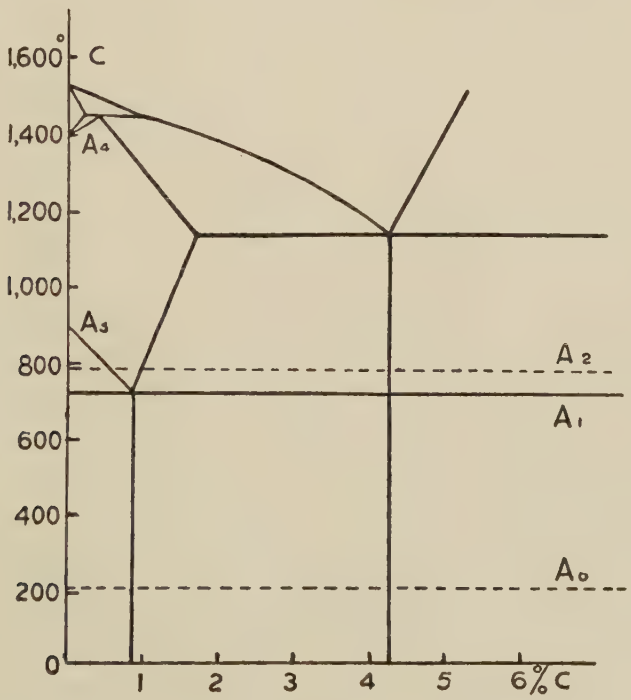


Fig. 409 — Honda's diagram.

CHAPTER XXVI

THE PHASE RULE

The phase rule to which references have been made in the preceding chapters should now be considered as it has been found of much assistance in interpreting correctly the iron-carbon equilibrium diagram.

Enunciation of the Phase Rule. — The phase rule was enunciated in 1878 by Willard Gibbs, at the time Professor of Physics in Yale University. It is one of the most notable contributions ever made to physical chemistry.

The phase rule deals with the *equilibrium* of systems and is generally expressed by the formula:

$$F = C + 2 - P$$

showing the relation existing between the *degrees of freedom* (F) of a *system*, the number of *components* (C), and the number of *phases* (P); it tells us that the number of degrees of freedom of any system is equal to the number of its components plus two, minus the number of phases present. In order to understand the phase rule and its application, it is necessary and sufficient to have an accurate understanding of the meaning of the terms employed in its enunciation, namely, equilibrium, degrees of freedom, components, and phases.

Equilibrium. — A substance or system may be said to be in a state of equilibrium when it is chemically and physically at rest, meaning by chemical rest that chemical compounds are neither being dissociated nor formed, and by physical rest, not the absence of motion but the absence of molecular transformation, such as changes of state or allotropic changes. It is necessary, however, to distinguish between *homogeneous* and *heterogeneous* substances. A substance is said to be homogeneous when it is chemically and physically uniform throughout, i.e. when any two portions of it possess identical chemical and physical properties. Homogeneous substances are necessarily gaseous mixtures, elements, chemical compounds, or liquid and solid solutions. The equilibrium of a homogeneous system is sometimes called homogeneous equilibrium. A heterogeneous substance is made up of two or more physically separate parts, that is of parts having different physical properties. Ice and water, many rocks, and many alloys are instances of heterogeneous substances. If the component parts of heterogeneous substances may be present in indefinite proportions, the substances are mechanical mixtures; if they occur in definite proportions, the substances are eutectic or eutectoid alloys. The equilibrium of heterogeneous systems is sometimes called heterogeneous equilibrium.

Howe has recently suggested that the homogeneous constituents of alloys be called "metarals" because of the great analogy between the constitution of metallic alloys and of rocks, the minerals being the homogeneous components of the latter, while the word aggregate is very frequently used to designate heterogeneous alloys. In metal-

lography, therefore, metarals and aggregates may conveniently replace the equivalent terms, homogeneous and heterogeneous substances, of the physical chemist.

Only three independently variable factors can effect the equilibrium of a system, namely, (1) the temperature, (2) the pressure, and (3) the concentration or composition. If arbitrary values may be given to one or more of these factors without destroying the chemical and physical rest of the system, its equilibrium is said to be *stable.* On the contrary, if a change in value of any one of these three factors results in chemical or physical transformation, i.e. in atomic or molecular activity, such as dissociation or formation of chemical compounds, changes of state, or allotropic changes, the equilibrium of the system is *unstable.* Water under atmospheric pressure is in stable equilibrium, for we may change its temperature within wide limits without causing it to undergo a change of state, while of course its chemical composition remains likewise unaffected. All elements are generally in a state of stable equilibrium, as well as an infinite number of substances composed of two or more elements, for they may be heated, for instance, through wide ranges of temperatures without upsetting their physico-chemical equilibrium. Examples of unstable equilibrium, however, are far from uncommon. During the solidification of substances, for instance, stages must generally be passed through during which the equilibrium of the substance is unstable, and it is often possible through very rapid cooling to retain in the cold the unstable conditions, because of the rigidity of the substance now opposing the changes needed for a return to stable equilibrium. It has been seen in these chapters that hardened steel is, for the above reason, unstable, hence the possibility of tempering it by slight reheating.

The kind of equilibrium known as *metastable* remains to be described. Liquids may be cooled, when taking the necessary precautions, below their normal freezing point without freezing, the phenomenon being known as superfusion, surfusion, or undercooling, and the substance being said to be in metastable equilibrium. Water, for instance, may be cooled below 0 deg. C. and still remain liquid. The introduction of a solid fragment of the substance, a piece of ice in the case of water, results in the solidification of the liquid, while its temperature rises to its normal freezing point. Otherwise, the substance may be kept liquid below its solidification point for any length of time. If the temperature of the liquid continues to fall, however, a point is reached when its equilibrium becomes *unstable,* i.e. when further lowering of temperature causes the liquid to solidify. To state the case broadly, the failure on the part of a system to undergo a certain chemical or physical transformation when that transformation is due, *although given the necessary time,* results in metastable equilibrium, while its failure to undergo a transformation *because of the necessary time being denied,* as in quenching, results in unstable equilibrium. Metastable equilibrium is stable, at least within narrow limits of temperature, while, theoretically at least, slight heating of a substance in unstable equilibrium should result in a partial return to a more stable condition, that is, in a partial occurrence of the transformation that was suppressed by quick cooling.

Degrees of Freedom. — By the degrees of freedom (sometimes called degrees of liberty) of a system is meant the number of the three independently variable factors, temperature, pressure, and concentration, which may arbitrarily be made to vary without disturbing the system's physico-chemical rest. It has already been noted that a system, in order to be in stable equilibrium, must have at least one degree of freedom. It will also be understood that no system can have more than two degrees of

freedom, because in the case of arbitrary values being given to two of the factors, the value of the third is necessarily fixed, this being due to the known rigid relations existing between temperature, pressure, and concentration.

Systems which have no degree of freedom are said to be "unvariant" or "nonvariant." Their equilibrium is necessarily unstable. Systems having one degree of freedom are called "univariant" or "monovariant," and those with two degrees of freedom "bivariant" or "divariant."

Phases. — By the phases of a system are meant the *homogeneous*, physically distinguishable, and mechanically separable constituents of that system. Water, ice, and vapor, for instance, are the possible phases of the water system; quartz, felspar, and mica are phases of granite, that is of the silica-alumina-potash system. It will be apparent that phases must necessarily be gaseous mixtures, elements, definite chemical compounds, or solutions. As previously mentioned, Howe, following the petrographical nomenclature, and noting that the minerals are the phases of rocks, calls "metarals" the phases of metals and alloys.

Components. — The components of a system are described by Findlay as "those constituents the concentration of which can undergo *independent* variation in the different phases," by Bancroft as "substances of independently variable concentration," by Mellor as those "entities which are undecomposable under the conditions of experiments," by Howe as "free elements and those compounds which in the nature of the case are undecomposable under the conditions contemplated, and so play the part of elements." The components of a system may be either chemical compounds or elements, but there is at times some difficulty in grasping the distinction between the components of a system and its ultimate chemical constituents. The criterion by which to decide whether an entity is or is not a component, is the possibility of independent variation in the different phases. Take the water system, for instance: evidently water and not hydrogen and oxygen is the component, because any variation in the proportion of hydrogen would necessarily imply a corresponding and well-defined variation in the proportion of oxygen and vice versa. Findlay writes:

"In deciding the number of components in any given system, not only must the constituents chosen be capable of independent variation, but a further restriction is imposed, and we obtain the following rule: *As the components of a system there are to be chosen the* **smallest number** *of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.*"

In the case of alloys, however, such difficulty does not arise, for the constituent metals are always the components of the systems.

The Phase Rule Applied to Alloys. — In dealing with alloys we may for all practical purposes ignore the influence of pressure, seeing that because of their feeble volatility they are practically always subjected to atmospheric pressure. Omitting the influence of pressure necessarily reduces by one the possible number of degrees of freedom, so that in the case of alloys the phase rule may be expressed by the formula:

$$F = C + 1 - P$$

signifying that the number of degrees of freedom is equal to the number of components plus one, minus the number of phases. Since to be in stable equilibrium a system must have at least one degree of freedom, it is obvious that an alloy made up of n metals cannot have more than n phases. If it had $n + 1$ phases it would have no

degree of freedom, that is its equilibrium would be unstable. With $n - 1$ phases it would have two degrees of freedom. It could not have less than $n - 1$ phases, since it cannot have more than two degrees of freedom.

The Phase Rule Applied to Pure Metals. — Pure metals have only one component, but their possible phases are (1) liquid metal, (2) solid metal, (3) several allotropic conditions of the solid metal. Let us consider Figure 410, which represents the solidification of a pure metal, as explained in Chapter XXV.

Above the temperature T the metal is entirely liquid; it has but one phase, and consequently one degree of freedom ($F = 1 + 1 - 1 = 1$). The system above T

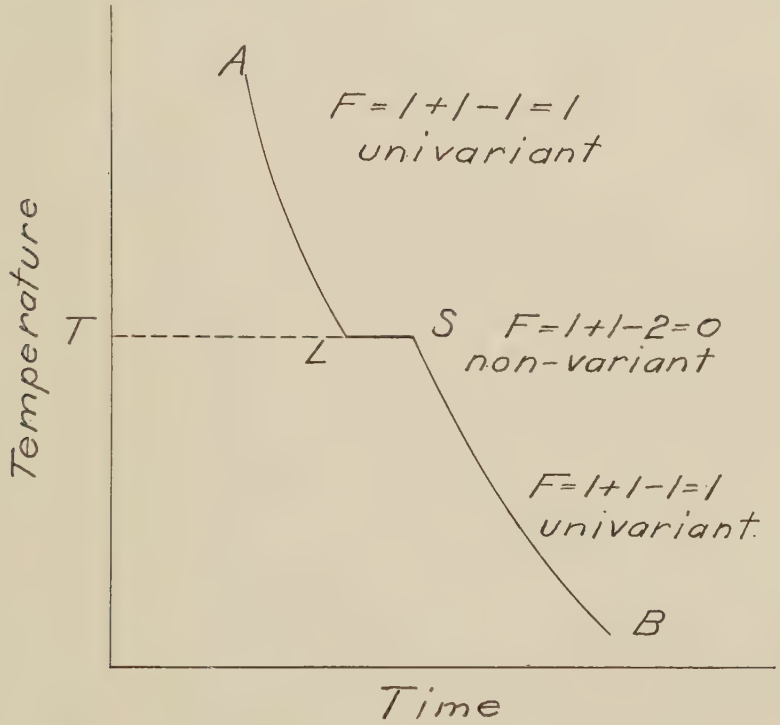


Fig. 410. — Equilibrium of pure metals according to the phase rule.

is univariant; its temperature may be altered within wide limits without disturbing its equilibrium: it remains liquid. At the temperature T two phases are present, solid metal and liquid metal, the metal having, therefore, no degree of freedom ($F = 1 + 1 - 2 = 0$): it is non-variant. Liquid and solid metal can exist only at one temperature, the critical temperature of solidification, any change of its temperature resulting in the disappearance of one of the phases, that is in a return to stable equilibrium. Increasing the temperature must result in the disappearance of the solid phase, while lowering the temperature must cause the disappearance of the liquid phase. Below the temperature T the system contains only the solid phase, being, therefore, univariant: its temperature may be varied arbitrarily.

The Phase Rule Applied to Binary Alloys. — Binary alloys having for components the two alloying metals, the formula of the phase rule becomes:

$$F = 2 + 1 - P$$

or

$$F = 3 - P$$

Clearly binary alloys when in a condition of stable equilibrium cannot have more than two phases. With one phase they will be bivariant, with two phases univariant, and with three phases non-variant. Let us apply the rule to the fusibility curves of binary alloys of metals partially soluble in each other when solid (Fig. 411). Above the liquidus MEM' there is but one phase present, namely the liquid phase, the system being, therefore, bivariant ($F = 3 - 1 = 2$), i.e. both temperature and concentration may be varied arbitrarily without upsetting the equilibrium of the system, which means, in the case under consideration, without causing its solidification. On reaching any point L of the liquidus the alloy begins to solidify, and two phases are now present, namely solid solution and liquid alloy, the system becomes univariant ($F = 3 - 2 = 1$). Having but one degree of freedom only, the temperature

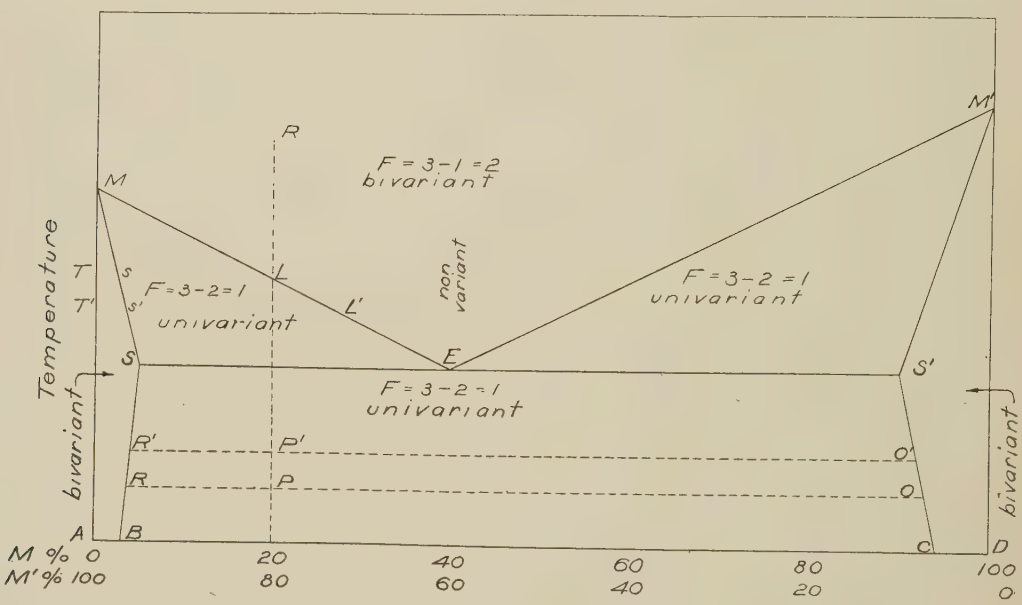


Fig. 411. — Equilibrium according to the phase rule of binary alloys whose component metals are partially soluble in each other in the solid state.

or the concentration may be *arbitrarily* varied. Should we, for instance, lower the temperature of alloy R from T to T' (Fig. 411) the composition of the liquid phase *necessarily* shifts from L to L', and that of the solid phase in equilibrium with it from s to s'. In the region $MSES'M'$ of the diagram bounded by the liquidus and solidus lines, therefore, the alloys are univariant, any arbitrary change of temperature resulting in a well-defined change of concentration and vice versa. At E, corresponding to eutectic composition and eutectic temperature, three phases are present, namely two solid solutions and liquid alloy, the system having no degree of freedom ($F = 3 - 3 = 0$). Neither the temperature nor the concentration may be altered without causing the disappearance of at least one of the phases. Increasing the temperature must result in the disappearance of both solid solutions, the system becoming bivariant, while lowering it must be followed by the disappearance of the liquid phase. Again, shifting the concentration to the left or right of E must yield the univariant system solid solution plus liquid. Clearly two solid phases and a liquid phase can only exist at one critical temperature and for one critical compo-

sition of the alloy; in the case of a eutectic alloy these three phases can exist only at its freezing temperature. In the areas $AMSB$ and $DM'S'C$ single homogeneous solid solutions only are present, that is, but one phase exists, and the corresponding alloys have, therefore, two degrees of freedom. Arbitrary changes both of temperature and composition within these areas do not disturb the equilibrium of the system. Within the region $BSS'C$ two phases occur, solid solution M and solid solution M', the corresponding alloys having, therefore, but one degree of freedom. Increasing the temperature from P to P', for instance, must result in shifting the composition of the solid solutions respectively from R to R' and from O to O'.

The Phase Rule Applied to Iron-Carbon Alloys. — Since iron-carbon alloys belong to the class of binary alloys the constituents of which are partially soluble in each other in the cold, the application of the phase rule to their equilibrium diagram should not present any difficulty, but we have now to consider allotropic changes as well as changes of state. Their possible phases or metarals are: (1) liquid iron, (2) liquid solution of carbon (or Fe_3C) in iron, (3) solid solution (austenite) of carbon (or Fe_3C) in gamma iron, (4) solid gamma iron, (5) solid beta iron, (6) solid alpha iron (ferrite), (7) solid solution (martensite)[1] of carbon (or Fe_3C) in beta iron, (8) solid cementite, (9) graphite, and possibly others. The exact nature of troostite and sorbite being still in doubt, they are not here classified as phases, seeing that they may be, and probably are, aggregates of two or more phases, unless indeed they be, according to Benedicks, emulsions or colloidal solutions. Scientists do not agree, however, as to whether colloidal solutions are or are not phases, opinions differing in regard to their homogeneity. Indeed some writers like Le Chatelier question the existence of colloidal solutions, which they consider as finely divided aggregates. Pearlite evidently is not a phase, but an aggregate of the two phases, ferrite and cementite, in constant proportion, after the fashion of eutectic and eutectoid mixtures.

Let us now apply the teachings of the phase rule to the iron-carbon equilibrium diagram (Fig. 412). The number and kinds of phases existing at different temperatures, and for different proportions of the components, iron and carbon, have been clearly indicated and will be readily understood in view of the foregoing considerations. Above the liquidus LEL' all alloys are composed of but one liquid phase, and have, therefore, two degrees of freedom; between the liquidus and solidus, that is in the region LSE and $L'S'E$, two phases are present, liquid solution plus solid solution (austenite), or liquid solution plus solid Fe_3C, hence the corresponding alloys have here but one degree of freedom; alloys of composition E and at the corresponding temperature are evidently made up of three phases, namely liquid solution plus solid austenite plus solid cementite, being, therefore, non-variant; in the region $LADS$ all alloys being composed of but one phase, namely solid austenite, are bivariant; at D the alloy contains three phases, ferrite, cementite, and austenite, and is, therefore, non-variant; in the area $DSS'F$ two phases are present, solid solution (austenite) plus cementite, and the system has but one degree of freedom. If, as is often the case, cementite is in this region decomposed into iron and graphite the alloys are for the time being non-variant, becoming again univariant on the complete disappearance of cementite. In the region ABH beta iron and austenite are present, the alloys having in consequence but one degree of freedom; in the region $BCDH$ alpha ferrite and austenite are present and the alloys, therefore, are univariant. Finally below

[1] All investigators do not agree as to the homogeneity, that is the phase-like character of martensite, some still regarding it as an aggregate.

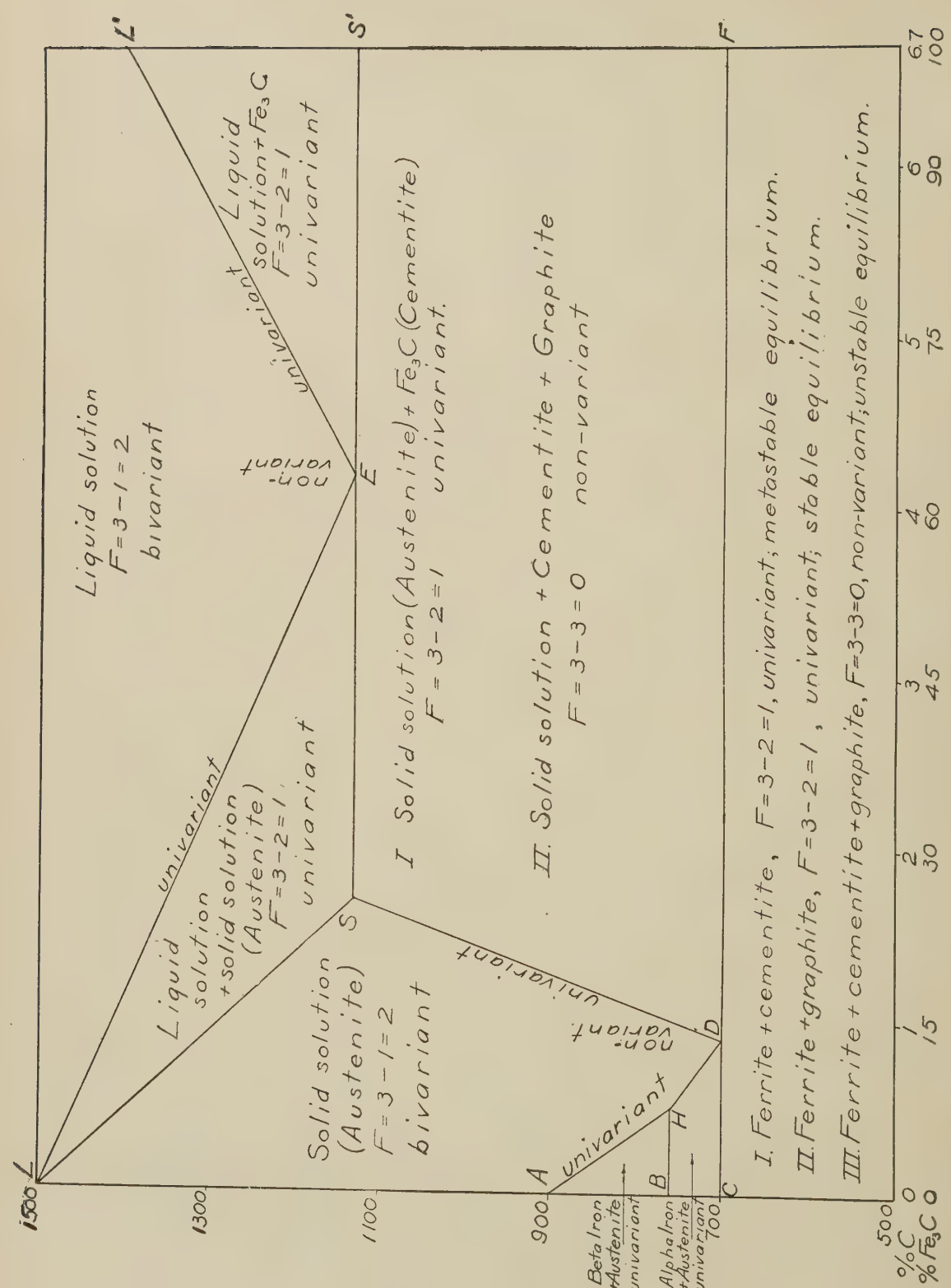


Fig. 412. — Equilibrium of iron-carbon alloys according to the phase rule.

CDF three possible cases should be considered: (I) the cementite formed during solidification and subsequent cooling remains unchanged, in which case the alloys are made up of the two phases ferrite and cementite, being, therefore, univariant, their equilibrium, however, as previously explained, is supposed to be metastable; (II) the cementite has been completely converted into ferrite and graphite, only those two phases being present, undoubtedly representing the stable equilibrium of all iron-carbon alloys; (III) the dissociation of cementite has been incomplete, both cementite and graphite being present, which with ferrite give three phases, the corresponding alloys being non-variant and, therefore, their equilibrium unstable. Condition (I) generally prevails in all grades of steel, and is readily produced in cast iron by rapid cooling, especially in the absence of considerable silicon, the resulting alloys being known as white cast iron. Condition (II) never obtains in steel, but may be produced in highly carburized alloys by very slow cooling through and below solidification, especially in the presence of much silicon and in the absence of manganese and sulphur. Condition (III) is the condition of the gray cast irons of commerce, which because of their composition and the conditions under which they cool contain both graphite and cementite.

APPENDIX I

MANIPULATIONS

The polishing, etching, and other treatments required to prepare samples of iron and steel for microscopical examination will be found described at some length in Appendix III in accordance with the recommendations of some committees.

To the beginner at least, the instructions given may appear somewhat complex and confusing. It is partly why the author ventures to describe briefly in the following pages the methods which he has found satisfactory. He hopes by doing so to be of service to some.

Size of Samples. — For convenience it is preferable that the samples to be microscopically examined should not exceed one inch square or round, in cross section, and three-fourths inch in thickness.

Cutting of Samples. — If the metal is sufficiently soft it can be cut readily with a handsaw or, preferably, with a power hack saw. If too hard, emery disks or diamond saws should be used. Suitable pieces of hard, brittle metals (white cast iron, spiegeleisen, etc.) may sometimes be obtained by breaking with a hammer.

Polishing. — The polishing operation may be divided into three steps: (1) grinding, (2) rough polishing, and (3) fine polishing. It may be performed (*a*) by hand, (*b*) by power, or (*c*) partly by hand and partly by power. Polishing by hand is necessarily more laborious and time-consuming but some believe that the results obtained are superior. When polishing, the sample should be pressed lightly upon the blocks and great care taken not to carry any coarse powder over a polishing block upon which a finer powder is used, as the presence of but a few coarser grains will greatly lengthen the operation. It is of much importance, therefore, to keep all the blocks carefully covered when not in use as well as the bottles containing the powders.

Grinding. — The preliminary grinding may be performed (1) by files of suitable fineness, (2) by emery or carborundum wheels, or (3) by emery papers. When using emery papers these may be fastened to wooden or other suitable supports and the grinding done by hand or the papers may be attached to revolving disks. Assuming the sample to have been filed with a smooth file or ground on a fine emery wheel, the author finds the use of No. 80 emery powder spread with water on wooden discs covered with linen cloth very satisfactory to remove the markings left by the file or emery wheel, replacing them with finer markings running at right angles to the former. If a sufficiently fine emery wheel has been used, however, it is often possible to proceed at once with the next step or rough polishing.

Rough Polishing. — The markings left by the file, the emery wheel, or emery papers should now be removed and replaced by finer ones, holding the sample at right angles to the markings it is desired to efface. This may be accomplished by the

use (1) of finer emery papers, (2) of fine emery powder, or (3) of tripoli powder or its equivalent.

The author finds the use of flour emery spread with water on disks covered with linen cloth followed by rubbing on tripoli powder spread wet on disks covered with broadcloth quite satisfactory. Some prefer to use two or more grades of French emery paper of increasing fineness for this rough polishing.

Fine Polishing. — The fine markings left by the rough polishing should now be removed by the use of a very fine polishing powder such as jewelers' rouge of the best quality, or specially prepared levigated alumina at present readily obtainable. The author uses these wet, on disks covered with fine broadcloth. When practical freedom from even microscopical scratches is essential, and also when it is desired to examine the occurrence of inclusions, the use of alumina is to be preferred to that of other powders. At this stage a magnifying glass is very useful for inspecting the specimen in order to ascertain whether it is ready for the etching treatment.

The specimen should now be carefully washed, and dried with a soft cloth, preferably a fine piece of old linen. Where an air blast is at hand, as is generally the case in chemical laboratories, it is advisable to dry the specimen with this blast (a hot blast is more effective than a cold one) instead of rubbing it with a cloth. The sample may then be rubbed gently once or twice on a piece of chamois leather stretched over a smooth piece of wood and carefully protected from dust when not in use, when it will be ready for the next or etching operation.

Polishing very Small Specimens. — For the polishing of samples too small to be conveniently held in the hand and also for preventing the rounding off of the edges the author, following Boylston's suggestions, uses small iron caps, known in the trade as "malleable gas caps," in two sizes, namely, $\frac{3}{8}$ inch and $\frac{1}{4}$ inch.

The cap used as a crucible is heated to about 200 deg. C. by placing it on an iron plate heated by a Bunsen burner. It is then filled with a fusible alloy recommended by Campion and Ferguson and consisting of 50 parts bismuth, 30 parts lead, 25 parts tin, and 3 parts zinc. This alloy melts below 100 deg. C., and if used in stick form the heated iron cap can readily be filled with molten alloy. The temperature of the cap and its contents is kept a little above 100 deg. C. and the specimen to be polished pressed into it. After solidification and cooling, which can be hastened by dipping in water, the whole is polished in the usual way.

By using iron caps instead of brass cylinders or other non-magnetic mounts the magnetic holders described on page 470 can be used with great gain in simplicity and convenience.

To make possible the polishing of very small specimens or for preventing the rounding of the edges of samples of moderate size, Le Grix uses small brass cylinders which he fills with gum lac and in which he presses the pieces to be polished (chips, cuttings, etc.). The whole is then polished as if it were a solid piece. The *modus operandi* is as follows: The brass mounting is heated in a Bunsen burner and filled with gum lac used in the form of sticks like sealing wax. After cooling, the excess gum is removed with a file to a level with the mount and the specimens pressed into the filling material by means of a preheated metallic blade. When the specimens are very small the polishing operation is very short indeed (Le Chatelier mentions 3 minutes). The etching reagent may be applied to the metallic particles by means of a glass rod, thereby preventing the brass mounting and even the gum from coming in contact with it, which is desirable since alcoholic solution would dissolve the latter.

The same material may also be used with advantage for filling up small cavities such as blowholes occasionally present in samples to be polished, thereby preventing the rounding of their edges or the tearing of the polishing cloths.

Polishing Machines. — A number of polishing machines are now available. Some have vertically, others horizontally, revolving polishing disks. Some consist of pol-

Fig. 413. — Belt-driven polishing machine.

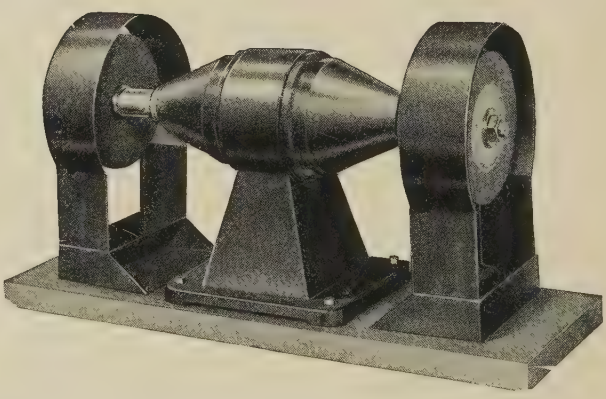


Fig. 414. — Polishing motor.

ishing motors, others are belt driven. Those most used in the United States are illustrated in Figures 413 to 418. Some prefer to build their own.

Polishing in Relief. — So-called relief polishing has been used successfully by Sorby, Martens, Behrens, and especially by Osmond. It consists in rubbing the specimen on a soft, yielding support with some suitable polishing powder, the softest constituents being, so to speak, dug out, leaving the harder ones standing in relief. These differences of level make it possible to distinguish the constituents under the microscope without further treatment. It is evident that only those samples which are made up of constituents differing much in hardness can be so treated. The free cementite of hyper-eutectoid steel or of white cast iron, for instance, can be made to stand strongly in relief because it is so much harder than the accompanying pearlite or other constituents.

Osmond polished his samples on a damp piece of parchment stretched over a piece of well-planed wood, and rouge was rubbed strongly on the parchment. The block

was then put under the tap and washed so that only those particles of rouge that had found their way into the pores of the parchment were retained. To distinguish between raised portions and cavities the luminous rays are strongly diaphragmed,

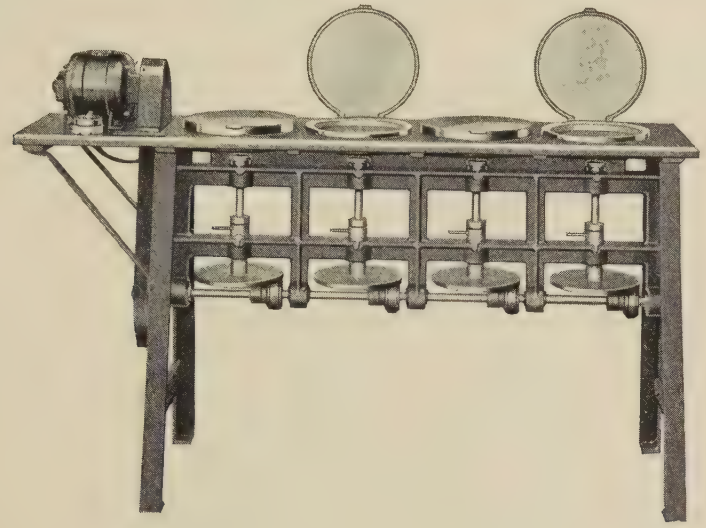


Fig. 415. — Warner & Swasey polishing machine.

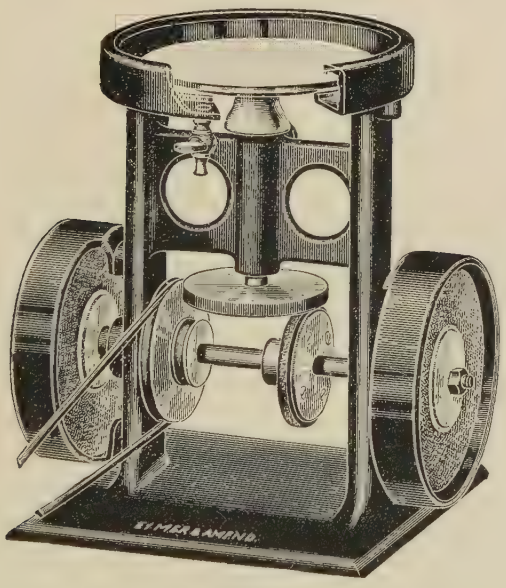


Fig. 416. — Wysor's grinding and polishing machine.

and the objective placed a little below the focusing point is slowly raised. The reliefs, which at first appear brilliant and yellowish on a relatively darker ground, gradually become dark on a bright ground; the cavities present inverse appearances so perfectly that two photographs of the same preparation, taken one a little below and the other a little above the mean focusing point, are almost positive and negative to one another.

Etching. — If the polished samples were now placed under the microscope it would be possible to detect the presence of inclusions such as graphite particles, slag, etc., and if a relief effect has been produced, the presence of constituents considerably

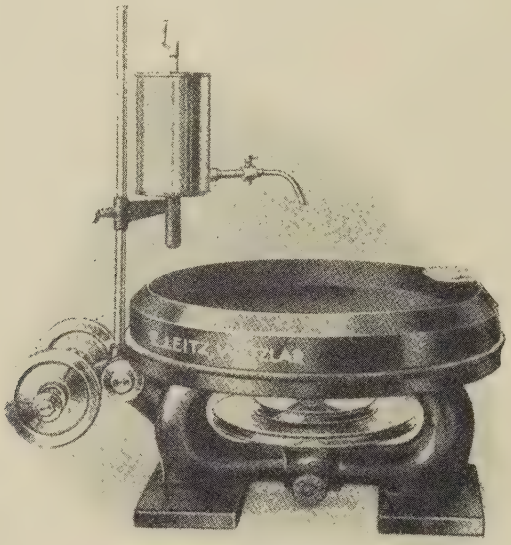


Fig. 417. — Leitz.

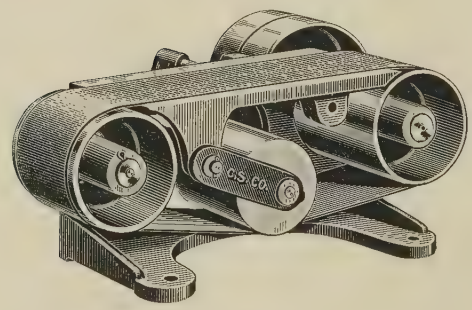


Fig. 418. — Grinding machine. Endless belt type, for rough grinding. Supplied with alundum or carborundum belts.

harder than the matrix (free cementite in hyper-eutectoid steel, for instance), but the structure of the metallic matrix itself would not be revealed, because its constituents being equally bright and exactly in the same plane would reflect the light to the same extent, after the fashion of a mirror. To make the structure apparent under the microscope it is necessary to impart unlike appearances to the constituents. This is generally accomplished by producing a slight corrosion or etching of the polished surface. For this purpose acid solutions are generally used, which attack some constituents more deeply than others or to the exclusion of others, an action which may or may not be accompanied by the deposition of some precipitated matter.

The action of these dilute acids is probably of an electrolytic nature, some of the constituents being electro-negative to others, hence the attack of some of these (electro-positive constituents) to the exclusion of others (electro-negative constituents) and the darker coloration of the former.

For the development of the microstructure of polished samples of iron and steel in general, the author's preference is as follows: (1) solution of nitric acid in alcohol, (2) solution of picric acid in alcohol, and (3) concentrated nitric acid.

Nitric Acid and Alcohol. — A solution should be prepared containing 5 per cent of concentrated, chemically pure nitric acid and 90 per cent of absolute methyl alcohol. A small amount of this solution should be poured in a glass or porcelain dish, preferably a small crystallizing glass dish with cover, and the sample immersed in it for 10 seconds, when it should be removed, conveniently with a pair of pincers (preferably with platinum tips), and washed in alcohol. The sample should now be dried, preferably by means of a blast. After rubbing the sample *very gently* once or twice upon a smooth piece of chamois leather stretched on a wooden block and carefully kept free from dust, it will be ready for examination. In case the etching is not sufficiently deep the treatment should be repeated.

Picric Acid. (Igevsky.) — An etching solution should be prepared containing 5 grams of picric acid, chemically pure, and 95 cubic centimeters of absolute alcohol. This should be kept in a well-stoppered glass bottle. The samples should be immersed in it for 30 seconds, washed in alcohol, dried, and the treatment repeated if necessary.

Concentrated Nitric Acid. (Sauveur.) — The polished specimen conveniently held with a pair of pincers (preferably with platinum tips) should be dipped in a beaker or other vessel containing concentrated nitric acid (1.42 specific gravity) and immediately afterwards held under an abundant stream of running water. When iron is immersed in concentrated nitric acid it assumes the passive state, that is it is not affected by it. As soon, however, as the layer of concentrated acid which covers the polished surface is diluted by the running water, the steel is vigorously attacked, but for so short a time (since the water soon removes all traces of acid) that there is little danger of etching too deeply. One such treatment is generally sufficient to bring out the structure sharply and clearly, but if the specimen is found insufficiently etched, the etching should be repeated in exactly the same manner. The author believes that the simplicity of this etching treatment and the excellent results generally obtained have been overlooked by metallographists.

Sodium-Picrate Etching of Cementite. — Cementite is not acted upon by the usual reagents employed for the etching of steel sections but remains brilliant and structureless. Kourbatoff, however, discovered a reagent which deeply colors cementite while leaving the ferrite unaffected, thus affording a sure means of distinguishing between the two. The treatment consists in immersing the polished sample in a boiling solution of sodium picrate in an excess of sodium hydroxide for some 5 to 10 minutes, when the cementite assumes a brown to blackish coloration. The etching solution may be prepared by adding 2 parts of picric acid to 98 parts of a solution containing 25 per cent of caustic soda, for instance 2 grams of picric acid in 98 cubic centimeters of a solution made up of 24.5 grams of caustic soda and 73.5 cubic centimeters of water.

Stead's Reagent for the Detection of Phosphorus Segregation in Iron and Steel. — For the detection of phosphorus segregation in iron and steel, Stead recommends the following method, which he considers superior to his heat-tinting method:

The reagent is made by mixing —

Cupric chloride	10 grams.
Magnesium chloride	40 "
Hydrochloric acid	20 cubic centimeters.
Alcohol to make up to . . .	1000 " "

The salts are dissolved in hot water to saturation and the solution made up to 1000 cubic centimeters with alcohol. Magnesium chloride is not necessary, but better results are, if anything, obtained by having it present.

"The specimens are simply covered with a thin layer of the reagent and must on no account be immersed in a bath of the liquid. The layer of liquid, after remaining on the surface for one minute, is shaken off and a second layer dropped on the surface and left there for the same period. This procedure is repeated as often as it is found desirable. The specimen is washed with boiling water, then with methylated spirits, and shaken to remove the spirit from the surface, the heat imparted by the boiling water rapidly evaporating the last traces of alcohol. The copper is usually left as a hard coherent layer, and is not readily removed by rubbing; indeed, the specimens may sometimes be repolished by rouged chamois leather without disturbing the deposited copper. The reagent not only indicates variations of phosphorus, but by progressive etching one can get a very good idea as to the degree of difference between the phosphorus in different portions of the same metal. If the reagent be applied in successive portions and the difference in the proportion of phosphorus be slight, as stated above, the copper invariably precipitates on the purer portion first; but on repeated application the copper gradually deposits also on the parts richer in phosphorus, and after many applications of the reagent the whole surface, including the phosphorized parts, becomes coated with copper. If, however, the phosphorus be very much concentrated in one or more parts, these remain perfectly bright and free from copper even after ten applications of the reagent."

Etching Wrought Iron. — The polished samples should be immersed for 10 or 15 seconds in a 5 per cent alcoholic solution of nitric acid or for 30 seconds in a 5 per cent alcoholic solution of picric acid, washed in alcohol, and dried with the usual precautions. Concentrated nitric acid may also be used.

The etching treatment should have outlined the joints between the ferrite grains clearly and sharply. If the structure lacks clearness it is safe to infer that the etching was not properly done. In that case the sample should be rubbed a few times on the chamois-leather block and again examined without repeating the etching. If the structure remains ill-defined, rub the specimen a minute or two on the rouge block or disk; wash, dry, and repeat the etching treatment until satisfactory results are obtained.

Should the boundaries of the ferrite grains appear too faint, the etching treatment should be repeated without repolishing, so as to etch these lines more deeply.

As the usual purpose of the microscopical examination of samples of wrought iron is to ascertain the quantity and mode of occurrence of the slag and the dimensions of the ferrite grains, it is not generally desired to etch the sample so deeply that some of the grains become deeply colored, still less that etching pits begin to appear.

As an experiment, however, it is advisable to etch samples of wrought iron gradually so that the different stages of the structure may be clearly seen: (1) before etching, slag fibers and a brilliant structureless matrix; (2) after a slight etching, ferrite grains sharply defined but remaining uncolored or but slightly colored; (3) after

a deeper etching, some of the ferrite grains deeply colored; and (4) after a still deeper etching, small cubic etching pits beginning to appear.

The production of these etching pits, however, is often a troublesome and uncertain operation. Heyn recommends for that purpose etching with double chloride of copper and ammonium, others (Stead) "a sufficiently long immersion in lukewarm 20 per cent sulphuric acid, followed by cleaning in nitric acid," or again (Le Chatelier) "an acidulated solution of ferrite chloride."

Etching Pearlitic Steels. — Pearlitic steels should be etched with the reagents already indicated, namely, nitric acid and alcohol, picric acid and alcohol, or concentrated nitric acid, the manipulations being the same as those prescribed for etching wrought iron. An immersion of 10 seconds in nitric acid or of 20 seconds in picric acid generally suffices. The contrast between the bright ferrite or brilliant cementite and the dark areas of pearlite should be very marked. If considerable free ferrite is present its grains should appear like a delicate but distinct network. The absence of this network is generally due to too slight an etching. Under high powers the pearlite should appear distinctly laminated, although it is not always possible to bring out the structure of every particle of that constituent.

Etching Sorbitic Steel. — The etching of sorbitic steel is similar to that of pearlitic steel both in regard to reagents used and manipulations, with the exception that sorbite generally etches somewhat more quickly than pearlite. Immersions of 7 or 8 seconds' duration in nitric acid or of 15 seconds in picric acid generally suffice. The sorbitic areas will have a granular but ill-defined structure.

Etching Troostitic Steel. — Troostite is etched more quickly and is more intensely colored than any other constituent of steel. For that reason very short immersions are advisable, namely, 2 or 3 seconds in nitric acid or 5 seconds in picric acid, or better still longer immersions in weaker acids (5 per cent nitric acid or 2 per cent picric acid). Such short etchings do not as a rule bring out the structure of the martensite which generally accompanies troostite, it being left white and structureless. To develop its structure deeper etchings are required.

Etching Martensitic Steel. — Martensite is colored more quickly than pearlite and sorbite but more slowly than troostite, hence the immersions of martensitic samples in the etching baths should be of relatively short duration, — 5 seconds in nitric acid or 10 seconds in picric acid. The acicular or zigzag structure of martensite should be brought out, but high power may be needed to resolve it.

Etching Austenitic Steel. — Undecomposed austenite is frequently present in hardened (martensitic) steel. It also occurs normally in certain alloy steels, as for instance in Hadfield manganese steel. When present in carbon steels its structure may be revealed by short immersions in nitric or picric acid. It generally remains bright while the martensite accompanying it is darkly colored. Some writers claim, however, that it may sometimes be colored darker than martensite. In the absence of much martensite its structure is polyhedral. Martensite is readily identified through its acicular or zigzag occurrence. The etching of austenitic alloy steels is further dealt with in the following paragraphs.

Etching Alloy Steels. — While the reagents and methods used for the etching of ordinary carbon steels are frequently effective for the etching of alloy steels, especially for those which after slow cooling become pearlitic, some of them are refractory to these treatments, much longer immersions being required to bring out their structures, while in a few instances the ordinary methods must be deeply modified.

According to some, manganese steels should be etched deeply in picric or nitric acid, washed in water, and dried without any attempt at removing the dark-colored films covering the surfaces of the specimens.

High-speed steel may be etched with nitric or picric acid alcoholic solutions of ordinary strength, but the time needed varies between a few minutes and more than an hour, according to the thermal treatment to which the specimens have been subjected, high heating followed by quick cooling generally requiring long immersions. In the author's laboratory, Mr. M. Yatsevitch has developed a very useful method for high-speed steel. Ten cubic centimeters of commercial hydrogen peroxide are mixed with 20 cubic centimeters of a 10 per cent solution of sodium hydrate in water. The steel samples are immersed in this solution for 10 to 12 minutes, washed first with water and twice with alcohol, and dried, preferably with a blast. The reagent should be prepared fresh every day. After the treatment indicated above the polished samples remain bright and their matrix structureless, but the free carbide containing tungsten is found to have been colored dark. While it is probable that other special carbides, such as carbide of molybdenum, would be likewise colored, no other constituent appear to be acted upon by this reagent, not even iron carbide (cementite). The method affords a means of bringing out clearly the amount of free carbide in high-speed steel and of distinguishing between it and other constituents.

Some alloy steels of the stainless class, such as high chromium or high nickel, may be etched with aqua regia or with aqua regia and glycerine.

Etching Cast Iron. — The etching of polished samples of cast iron is conducted in every respect like the etching of steel specimens. To bring out clearly the phosphide eutectic and to prevent its being mistaken for pearlite areas or vice versa, the heat-tinting method devised by Stead is very useful. Polished samples of gray cast iron should generally be first examined before etching, the distribution, size, and form of the graphite particles being then more clearly revealed.

Etching for Macrostructure. — A number of formulæ have been suggested for etching reagents suitable for revealing the macrostructure of iron and steel caused by persistent dendritic segregation. They all contain some copper salt, which causes the selective deposition of copper on some portions of the specimen. The structures revealed are dendritic in the case of castings, and banded in the case of forgings. The reagent preferred by the author is known as Le Chatelier No. 1. It has the following composition:

Methyl alcohol	100 cubic centimeters
Water	18 " "
Hydrochloric acid	2 " "
$CuCl_2$	1 gram
$MgCl_2$	4 grams

Other reagents are described in Appendix III

Historical. — Sorby etched his specimens with very dilute solutions of nitric acid in water and this reagent was widely used for many years by other metallographists. The water has now been replaced by absolute alcohol. Le Chatelier has mentioned the use of glycerine as a satisfactory non-oxidizing vehicle for nitric as well as for picric and hydrochloric acid.

Osmond, the author believes, was the first to use tincture of iodine. This tincture is applied in the proportion of one drop per square centimeter of surface and allowed to act until it is decolorized, the treatment being repeated after examina-

tion if needed. Le Chatelier recommends applying the tincture with the tip of the finger and gently rubbing the specimen.

Stead used a solution made up of 1.25 grains of iodine, 1.25 grains of iodide of potassium, 1.25 grains of water and alcohol to make up 100 cc. After the iodine has lost its color the sample should be washed in water, then in alcohol, and finally dried in a blast of hot air.

Martens and Heyn in 1904 recommended the use (1) of an etching solution containing 1 part of hydrochloric acid (1.19 sp. gr.) and 100 parts of absolute alcohol and (2) of 1 part of hydrochloric acid in 500 parts of water with the assistance of the electric current.

Heyn used a solution of double chloride of copper and ammonium containing 12 grains of the salt and 100 grains of distilled water.

To distinguish with certainty between iron phosphide and cementite, Matweieff recommends *neutral* sodium picrate washed several times with distilled water to eliminate the excess of picric acid or of sodium that might be present. The sample is immersed in the boiling solution for 20 minutes, a treatment by which the iron phosphide is strongly attacked while the cementite and pearlite remain unaffected.

For etching austenite and martensite Robin recommends the use of a saturated solution of picric acid in alcohol, an immersion of 30 seconds to 1 minute, washing with water without touching the specimen, and drying by air blast or simply in air. Films of various tints are formed, ferrite remaining uncolored.

Le Chatelier has used bitartrate of potassium as an etching reagent. It leaves cementite and pearlite uncolored, while it imparts a dirty coloration to ferrite.

The same author has described the use of a freshly prepared reagent made up of equal parts of a solution containing 50 per cent of soda and of a solution containing 10 per cent of lead nitrate. Cementite is quickly colored by it while the phosphides, and especially the silicides, are also attacked. The reagent is recommended for highly carburized metals. Medium high carbon steels of great purity are not affected by this solution, but when impure, the pearlite is energetically acted upon, probably because of the presence of impurity in that constituent.

Le Chatelier has also mentioned the use of a solution of 10 per cent gaseous hydrochloric acid in absolute alcohol to which is added 5 per cent of cupric chloride for annealed steels and 1 per cent of the same salt for hardened steels. Ferrite and cementite are not colored, martensite very little, austenite a little more, troostite and sorbite decidedly.

The etching reagents usually applied to bring out the structure of unhardened steel, namely, picric acid, nitric acid, tincture of iodine, etc., do not always yield satisfactory results in the case of hardened steel. Kourbatoff discovered a complex reagent which often produces greater contrasts between the various constituents. It is made up by mixing 1 part of amyl alcohol, 1 part of ethyl alcohol, 1 part of methyl alcohol, and 1 part of a 4 per cent solution of nitric acid in acetic anhydride and should be prepared just before use.

Heyn recommends for etching hardened steel a solution containing 1 part of hydrochloric acid and 99 parts of absolute alcohol. More uniform results are obtained if a weak current of electricity be passed through the solution, the samples to be etched forming the positive pole while the negative electrode may consist conveniently of a piece of sheet lead. With the assistance of the electric current the use of a very

dilute aqueous solution is advisable, namely, 1 part of hydrochloric acid in 500 parts of distilled water.

Osmond, likewise, used successfully a solution of 10 per cent of hydrochloric acid in water by which the martensite is colored darker than austenite, the treatment requiring several minutes. Osmond writes: "There is more regularity obtained by having the specimen connected, by means of a platinum wire, with the positive pole of a bichromate cell, a strip of platinum placed in the acid being connected with the negative pole. In this way the specimen becomes the anode, and the platinum the cathode."

Benedicks recommends for the etching of martensito-austenitic steel a 5 per cent alcoholic solution of metanitrobenzol-sulphonic acid which always darkens martensite more than austenite. Immersions of some 15 seconds are generally sufficient.

Hilpert and Colver-Glauert have described the use of sulphurous acid for non-pearlitic steels and for pig iron. A saturated solution of sulphur dioxide in water is prepared and 3 or 4 per cent of that solution in water used. The time of etching varies between 7 seconds and 1 minute. Alcohol may be substituted for water, in which case the etching lasts several minutes. The treatment causes the deposition of layers of iron sulphide of different thicknesses and, therefore, of different colors, on the various constitutents.

Rosenhain and Haughton report interesting results obtained with a solution made up as follows:

Ferric chloride 30 grams, hydrochloric acid (conc.) 100 cubic centimeters, cupric chloride 1.0 gram, stannic chloride 0.5 gram, water 1 liter.

The polished specimen, which should be absolutely clean, is immersed in the solution for 10 seconds to 2 minutes according to the character of the metal. The action of the reagent consists in the deposition on the surface of the steel of thin films of metallic copper which vary in thickness, and therefore in appearance, with the various constituents present, producing an effect not unlike that obtained with heat tinting. The authors write that "in practically pure carbon steels the new reagent yields a pattern which is the reverse of that obtained with the ordinary etching reagents, such as picric acid, ferrite being darkened while pearlite remains white; on hardened steels, especially those of low and moderate carbon contents, the reagent yields very clear results, particularly in the etching of martensite, although in this case the patterns are not reversed as compared with those obtained with picric acid, sulphur dioxide, etc. The principal interest and importance of the new reagent, however, lies in the fact that it reveals in a clear and striking manner the distribution of phosphorus, particularly in mild steels."

Howe, according to O. F. Hudson, used in his laboratory Heyn's reagent (10 per cent copper ammonium chloride in water) for low carbon iron and steel. He found that it "shows grain boundaries readily, rather obscures Neumann lines," and that it is the best reagent for etching figures and pits. Hoyt uses a similar solution "principally for microscopic examination of low carbon steel, wrought iron, white cast iron, and in the determination of phosphorus segregation in wrought iron."

Le Chatelier was one of the first to advocate the use of the electric current in order to obtain a more uniform action in etching iron and steel samples. Sheet lead may be used for the positive electrode, and, as electrolyte, a 10 per cent solution of chloride or sulphate of ammonium gives good results. The current needed varies between 0.001 and 0.01 amperes per square centimeter.

Electrolytic etching has been described by Cavalier (1909). A few cubic centimeters of the electrolyte are placed in a platinum dish *C* (Fig. 419) connected with one pole of the battery *P;* the specimen *E* connected with the other pole is placed in the solution, a piece of filter paper *A* being inserted between the dish and the polished surface of the specimen. The current is regulated through the rheostat *R.* Four or five volts are required with an intensity of 0.001 to 0.01 amperes per square centimeter. The attack lasts from a few seconds to a few minutes.

Steel while at a high temperature (red heat) has been etched (1) by Saniter in molten calcium chloride heated to the desired temperature, and (2) by Baykoff in a current of gaseous hydrochloric acid. It may also be etched in a current of hydrogen.

Washing and Drying. — After removing the specimens from the etching bath, the author washes them in alcohol and dries them in an air blast. Washing in water, in

Fig. 419. — Arrangement for electrolytic etching.

caustic potash, in lime water, and in ether has also been recommended as well as the use of fine linen cloth and of a hot blast for drying.

Preserving. — The author preserves his etched specimens in desiccators and in air-tight cabinets.

Several protective coatings have been described. Stead covers them with paraffin wax dissolved in benzol which is removed by wiping with a clean linen rag moistened with benzol when it is desired to examine the specimens. Le Chatelier applies a coating of "zapon," a solution of gun cotton in amyl acetate sufficiently transparent to allow examination with the highest powers.

Heat-Tinting. — Heat-tinting is described by Stead, its originator, as follows: "Heat-tinting consists in heating polished specimens of metals until their surfaces become colored by oxidation films.

"Alloys of iron and phosphorus, and commercial steel, contain part of their mass richer in phosphorus than other portions. In fact the iron and the phosphide are seldom intimately mixed in ordinary steel. When polished specimens are placed on the surface of a molten bath of tinman's solder,[1] and the heat gradually raised, the portions of the specimens richest in phosphorus assume oxidation tints earlier than the purer parts; hence it follows that by the time the phosphorus-rich parts have passed through the transition stages of yellow-brown to red and purple, the purer portions will have reached the yellow-brown or red stage, and if at this point the specimen be removed from the source of heat, the phosphorus-rich portions will appear under the microscope as purple or blue on a yellow-brown or red background. If the heating of the specimen be continued, the phosphorized part will assume a yellowish-white tint, while the purer part will reach the blue stage. Each part will pass through the complete range of color from yellow to blue and then to nearly white, but not at the same time, because the purer portions always lag behind, the degree of lag depending on the variation in the proportions of phosphorus in the different parts.

[1] An iron plate heated by a Bunsen gas burner may be used instead. (Author.)

"Heat-tinting is also useful in intensifying the difference in color between ferrous sulphide and manganese sulphide when present together in steel. On heating polished metal containing inclusions of each sulphide until it appears to assume a uniform brown tint, the ferrous sulphide, which is naturally pale yellow, will be found under the microscope to have been colored purple, while the manganese sulphide, naturally a pale dove color, will have become white. If the heating be continued until the surrounding metal becomes blue, the ferrous sulphide will be blue and the manganese sulphide yellow.

"To obtain good results by heat-tinting, it is absolutely necessary first to apply to the surface a very dilute solution of some acid in alcohol. Picric acid answers admirably, but care must be taken to remove the solution employed before it has time to develop the pearlite or sensibly to etch the metal. After thoroughly washing the specimen in water, it is dried with a perfectly clean rag and heated on a hot plate to about 150 deg. C. It is again rubbed with a warm clean cloth, and is then ready for heating to produce the color tint.

"It is difficult to explain why the preliminary acid treatment is necessary, but that it is so is proved in practice, for if it is omitted, the tinting is always unsatisfactory. It is possible that, during polishing, some of the softer metal becomes spread over the harder part, forming an exceedingly thin layer. This, however, is only a surmise."

Sulphur Printing. — The presence of sulphur in steel, especially when segregated, can be sometimes clearly revealed by a laboratory test known as "sulphur printing." As first described by Heyn and Bauer, it consisted in pressing upon the previously polished steel surface strips of silk impregnated with mercuric chloride and hydrochloric acid (10 grams mercuric chloride, 20 cubic centimeters of water, and 100 cubic centimeters of hydrochloric acid). The reaction between the acid and the sulphides wherever present generates H_2S (sulphureted hydrogen) which in turn reacts with the mercury salt producing stains of mercury sulphide varying in intensity according to the amount of sulphur present in the steel and revealing the spots where the latter occurs.

A better method (Baumann) consists in substituting for the silk ordinary silver bromide (photographic) paper moistened with dilute sulphuric acid, the generated H_2S producing dark stains on the paper where metallic sulphides were present in the steel.

The following more explicit instructions may be followed with good results. The sample to be tested should be filed flat and rubbed on two or three grades of emery paper, finishing with French paper No. 0. Sheets of Velox printing paper or its equivalent should be soaked until saturated in dilute sulphuric acid (2 per cent solution). The paper should then be placed on a piece of plate glass and the steel specimen, after washing it in clear water, gently pressed upon it for some 20 seconds, when it should be removed and the paper placed in sodium hyposulphite to remove the excess bromide, washed and dried. While theoretically areas containing phosphorus should also darken the bromide paper Stead reports that the staining from this cause is almost imperceptible.

Law covers the steel section with a coating of gelatine containing an acid solution of lead, mercury, or cadmium salt; the acid decomposes the iron or manganese sulphides and the resulting H_2S reacting with the lead or cadmium salt produces brown or yellow stains of lead, mercury, or cadmium sulphide. Rohl writes: "Care should be taken that the gelatine be as thick as possible, so as to be stiff enough to avoid its

flowing off or shifting its position after being applied. The gelatine should be applied hot to the slide by means of a glass rod. This method permits of testing under the microscope, for its sulphidic nature, an enclosure placed in the microscope and observed thereon, the stage being screwed back for the purpose of applying the gelatine, so that the place observed by the eye may be at once observed again in the microscope. Weak magnification has been found sufficient and practical for this purpose."

F. Rogers describes a method for taking sulphur prints of *fractures*, consisting in the use of a gelatine emulsion of silver bromide coated upon a very stiff grease clay and soaked in a dilute acid solution containing also a toughening agent. This emulsion is immediately pressed into contact with the clear fracture for a few seconds and withdrawn.

According to Rohl, ferrous sulphide is considerably darkened by 1 per cent solution of organic acids in ethyl alcohol, after 5 minutes' etching, as compared with

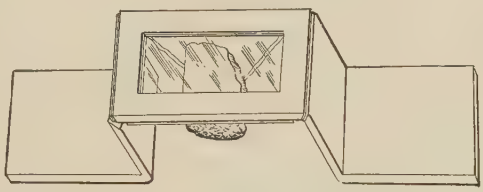


Fig. 420. — Specimen holder.

manganese sulphide. The same author writes that after a short preliminary etching with alcoholic solutions of organic acids (preferably picric acid), the successive tempering to dark yellow leaves the ferrous sulphide blue and the manganese sulphide a dull whitish. The reaction appears to be well adapted for distinguishing between the sulphides.

Specimen Holders. — In order to examine a piece of metal under the microscope, it is of course necessary that the polished and otherwise prepared surface be held in a plane accurately perpendicular to the optical axis of the instrument. This may be accomplished by so shaping the sample that it will have two sides exactly parallel, and preparing one of them for microscopical examination. This operation, however, is at best tedious and laborious, and metallographists have endeavored to replace it by the use of more or less ingenious devices for holding the specimens in the proper position. Some embed their samples in wax or in some other plastic material, while others have recourse to stages provided with special leveling devices.

The simple holder shown in Figure 420 gives better satisfaction, requiring no mounting whatever of the samples. The specimen, no matter how irregular in shape, is held firmly in place by a rubber band and the holder placed on the stage like an ordinary slide. If the correction of the objective demands it, a cover glass may be inserted between the sample and the holder. It will be apparent that the required manipulations are very simple and quickly performed.

A still simpler and more effective device can be used to hold in place samples of iron and steel and other magnetic substances. The device consists of a V-shaped permanent magnet of special steel about 1 inch wide and 2½ inches long (Fig. 421). This little magnet is placed on the stage of the microscope like an ordinary glass slide (Fig. 422) and the samples to be examined suspended to it from below, being held in place by the attraction of both poles. Small samples are suspended near the small

end of the V-shaped opening, while larger ones are placed nearer the wider end of the opening. This holder, therefore, is universal in its application within the limits of samples of suitable size for misroscopical examination. Its beveled edges make its use possible with high-power objectives and small specimens. If the opening of the

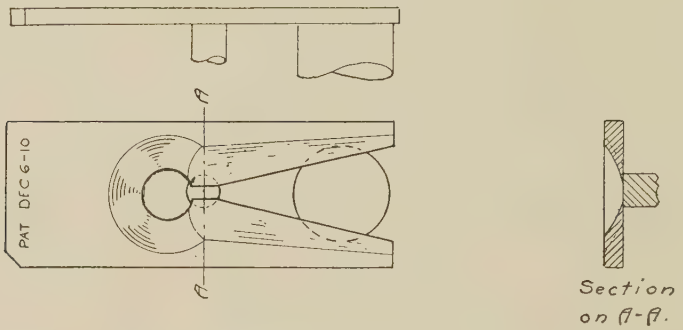


Fig. 421. — Magnetic specimen holder with large and small specimens.

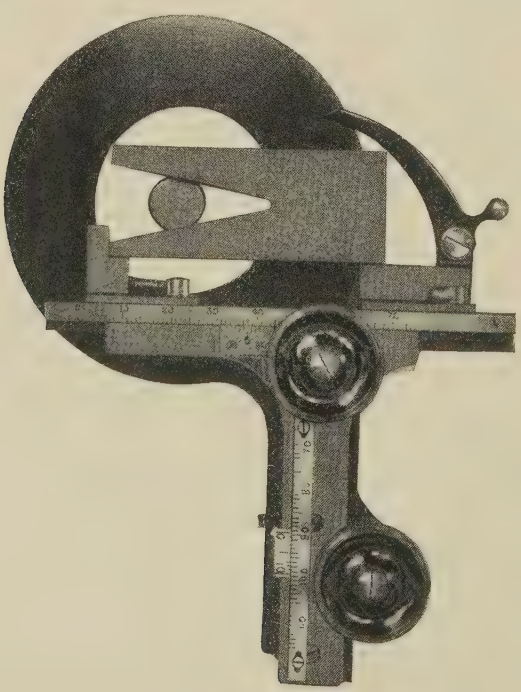


Fig. 422. — Mechanical stage to fit metallurgical microscope, magnetic specimen holder, and specimen.

stage be sufficiently large, say 1¼ inches or more in diameter, the magnet may be kept permanently on the stage, as the samples may then be readily removed or attached to the magnet with the fingers from below the stage. This adds so much to the convenience of this little device that it is strongly urged, in case the central aperture of the stage is too small, to have it suitably enlarged.

Finally, by placing the sample below the stage and bringing the prepared surface on a level with the stage, considerably greater working distance is secured, a gain which has its importance. When inverted microscopes are used, holders, of course, are not required.

Plastic Mounting. — Osmond mounted his specimens by embedding them in a little soft wax placed upon a glass plate. The leveling is managed by means of two pieces of glass tube of equal height, one on each side of the sample.

Stead places the specimens polished face down on a piece of plate glass (Fig. 423) and surrounds them with brass cylinders accurately turned. A piece of plastic wax is stuck upon the center of a glass microscope slide and is then pressed upon the sec-

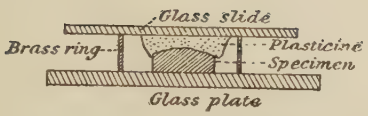


Fig. 423. — Stead's mounting device.

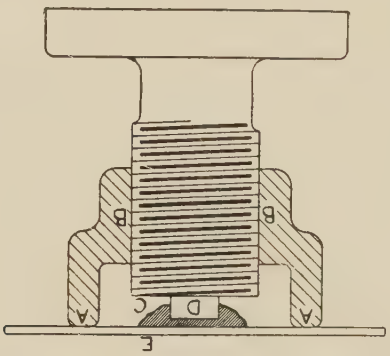


Fig. 424. — Gulliver's mounting device.

tion till the glass slide comes in contact with the brass ring. The specimen adheres to the wax and the mounting is complete.

Gulliver (1908) describes the device (Fig. 424) for mounting specimens. It consists of a circular ring faced on its upper surface *A*, and screwed internally at *B* to fit the foot, of which the upper end *C* is also faced. The distance between the parallel faces *A* and *C* can thus be adjusted. The specimen is placed at *D* and a glass slide *E* with some soft modeling clay or wax is pressed upon it until the glass touches the ring at *AA*.

Examination. — The source of light and condensers should be adjusted so that a beam of light of suitable size enters the vertical illuminator; the light beam should cover a little more than the aperture of the illuminator. A 2-in. (5X) eyepiece and a 16-mm. (⅔-in.) objective will be generally a satisfactory combination for the first examination. The image of the specimen should be focused roughly by the rack and pinion motion of the stage, and the milled head of the vertical illuminator turned tentatively and gently right and left until the sample appears brightly and uniformly lighted. The object should now be brought to a sharp focus by means of the fine adjustment.

As previously stated, if the structure lacks clearness it is safe to infer that the etching was not properly done. In that case the sample should be rubbed a few times on the chamois-leather block and again examined without repeating the etching. If the structure remains ill-defined, rub the specimen a minute or two on the rouge block or disk, wash, dry, and repeat the etching treatment until satisfactory results are obtained.

Examinations with high-power objectives (4 mm. or higher) require greater care and more delicate manipulations. It is especially for high-power work that the plain disk illuminator is superior to the prism type.

The specimens should be examined systematically over their entire surfaces, for which purpose a mechanical stage is invaluable, in order to judge of the uniformity or lack of uniformity of its structure. It should be borne in mind that the portions of heat-treated specimens corresponding to the outside of the original samples are very likely to be decidedly lower in carbon owing to the decarburizing atmosphere generally present in heating furnaces. It is often advisable first to examine the specimens before etching for the presence of slag or other enclosures, graphitic or temper carbon, minute blowholes, etc., these being more readily detected in the unetched condition.

In studying the structure of forged or rolled samples, specimens should generally be prepared corresponding to their cross sections as well as to their longitudinal sections, in order to detect any possible distortion or orientation of structure caused by the forging or rolling.

Photomicrography. — After having selected the spot to be photographed, light-tight connection should be established between the microscope and the camera (in some models the camera and misroscope are permanently connected) and the light carefully adjusted so as to obtain on the screen of the camera as bright and even an illumination as possible. The image should now be focused as sharply as possible, using a focusing cloth if necessary and gently turning the fine adjustment screw of the stand. A focusing glass may be used with great advantage for this operation and is of special importance when photographing with high-power objectives. It should be placed on the plain glass circle which occupies the center of the screen of the camera, and the image focused while being viewed through this lens. By this means we magnify the image formed upon the camera screen, and are therefore able to focus it more sharply in its finer details. Considerable light, however, is lost and the object will often appear but dimly lighted. The rule is to secure the clearest possible image while working tentatively the fine adjustment in both directions, bearing in mind that, at its best, the image may appear blurred and dimly lighted.

An ordinary eyepiece may be used in place of a focusing glass with, in many cases, satisfactory results.

Exposure. — After the image has been properly illuminated and focused the sensitive plate should be introduced and exposed, with the ordinary precautions, for a suitable length of time. The required time of exposure will vary according to (*a*) the kind of photographic plate used and (*b*) the amount and nature of light reaching the plate, which in turn will depend upon (1) the nature of the prepared surface, especially its power to reflect light, (2) the kind of illumination used, (3) the opening of the diaphragm or diaphragms controlling the amount of light allowed to reach the plate, (4) the kind of light filters used, if any, (5) the resolving and magnifying powers of the combination of objective and eyepiece used, and (6) the distance between the screen of the camera and the object.

Specimens which after etching remain quite bright naturally reflect more light and consequently require for their photography a shorter time than duller specimens. Generally speaking the higher the magnification the less light, hence the longer the exposure. The use of colored screens or solutions (light filters) as a rule lengthens the exposure considerably. By placing the screen of the camera at a greater distance from

the object (i.e. by extending the bellows of the camera) the magnification is increased but with accompanying loss of light and, therefore, increased length of exposure.

When using an arc light, orthochromatic plates, a special green screen, the illuminator diaphragm being wide open, the shutter diaphragm closed at 7.5, and the distance between the upper lens of the eyepiece and the screen of the camera being 385 mm., the following exposures in seconds for various combinations of objectives and eyepieces will generally yield satisfactory results:

EXPOSURE AND MAGNIFICATION TABLE

Eyepieces (magnification when used as magnifiers)

Objectives (equivalent focal length in millimeters)	5 ×	6.4 ×	7.5 ×	10 ×	12.5 ×	15 ×
32	5 (25)	7 (35)	9 (40)	11 (50)	13 (65)	15 (80)
16	7 (75)	10 (100)	12 (115)	15 (150)	18 (190)	20 (235)
4	15 (310)	20 (425)	25 (500)	30 (650)	35 (825)	40 (1000)

Exposure in Seconds

(Numbers between parentheses indicate approximate magnification in diameters.)

Diaphragms and Shutters. — It is sometimes advantageous to be able to control the pencil of light entering the illuminator with a view of securing sharper definition. To that effect an iris diaphragm suitably mounted should be placed between the condensing lens or lenses and the vertical illuminator. Some sort of an automatic shutter is convenient to control the exposure of the plates. This shutter may advantageously be combined with the iris diaphragm. Instead of being placed between the source of light and the vertical illuminator, diaphragms and shutters are sometimes inserted between the camera and the microscope. The best disposition consists in placing an iris diaphragm between the condensing lenses and the vertical illuminator, thus controlling the amount of light entering the latter, and another diaphragm combined with automatic shutter between the camera and microscope tube.

Monochromatic Light. — The different sources of light used for microscopical work yield white light, and since the correction, even of apochromatic objectives, for chromatic aberration is never perfect, it is evident that the use of monochromatic light, i.e. light of one wave length, is theoretically preferable, especially for photographing.

Monochromatic light may be obtained in two ways: (*a*) by using a source of light actually monochromatic, and (*b*) by causing white light to pass through colored glass screens or colored solutions (light filters), preventing the passage of some undesirable rays. The mercury arc lamp yields a nearly monochromatic light and has been tried by Le Chatelier with satisfactory results. It seems more convenient, however, when monochromatic light is wanted, to use light filters of suitable colors, in which case colored glass screens will be found easier to manipulate than glass cells containing colored solutions. The author recommends a special green screen supplied by Nachet of Paris or its equivalent, the Wratten B screen.

Photographic Plates. — The use of orthochromatic plates together with a suitable screen is recommended.

Development. — Formula and directions accompany each box of plates, and the student could not do better than to follow them faithfully.

Printing. — Any satisfactory photographic paper may be used, the printing and developing being conducted in the usual way. Drying on ferrotype plates affords a quick means of finishing the prints and giving them a satisfactory luster. It is recommended to trim the prints round 2 to 2½ inches in diameter, by means of a margin trimmer and suitable circular forms, as this will give them a very neat appearance.

APPENDIX II

THE OPTICS OF METALLOGRAPHY[1]

By W. L. Patterson

OBJECTIVES

The objectives undoubtedly constitute the most important part of the microscope. Their quality determines the final results.

The objective is so called because it is nearest to the object. Figures 425, 426, and 427 show respectively the 16, 4, and 1.9 millimeter objectives of the usual type, but they are made in a variety of focal lengths, numerical apertures, and styles of mount by various makers. Following are given the usual focal lengths and numerical apertures (N. A.) of achromatic objectives:

Focal Lengths Millimeters	Numerical Aperture (N.A.)	Type of Lens
32	0.10	Single achromatic lens
16	0.25	Two achromatic doublets
8	0.50	These three have non-achromatic front with two achromatic doublets
4	0.85	
3	0.85	
1.9	1.25	6 lenses in all
1.9	1.32	Fluorite construction, semi-apochromatic

Further reference will be made to the apochromatic objectives later. The focal length of an objective does not indicate its working distance, but means that the combination of lenses composing the objective is equal in focus to a single lens of the stated focus. Thus the working distance for the —

16	millimeter	focus	= 7	millimeters
4	"	"	= 0.30	"
1.9	"	"	= 0.15	"

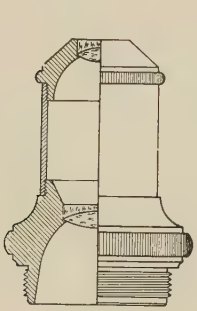
An objective may be said to possess seven qualities: magnifying power; aperture, or numerical aperture; resolving power; depth of focus, or penetrating power; illuminating power; flatness of field; and defining power. To fulfill all of these requirements in a satisfactory manner necessitates considerable skill upon the part of the optician. These qualities will be discussed one by one.

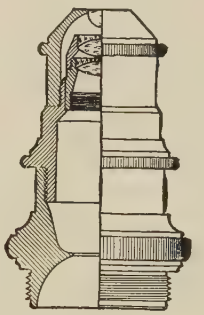
Magnifying power usually is stated in the catalogues of various makers in terms of the combination of a certain objective, certain eyepiece, and tube length at a predetermined image distance. While tables given in the catalogues are approximately

[1] Mr. W. L. Patterson has kindly revised for the present edition of this book his excellent paper on the "Optics of Metallography," presented to the American Society for Steel Treating (Vol. II, No. 2, 1921). It is reproduced here with the permission of that society.

correct, the magnification stated will be obtained only if the conditions given are fulfilled. If the tube length, that is the distance between objective and eyepiece, is increased or decreased, or an increase or decrease in image distance is taken as in photography, the magnification tables will not prove correct. Tables given in catalogues are often for visual work and are based on an apparent or virtual image being formed in space at a distance of 250 millimeters from the eye. This apparent size will vary with persons having near- or far-sighted eyes, but the normal distance is taken as 250 millimeters and the size of the image is the same if projected on the ground glass of a camera at 250 millimeters.

Makers of objectives also give in their catalogues the initial magnification of their several objectives, that is the magnification they give at a certain distance unaided





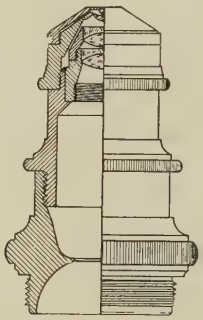


Fig. 425. — 16-millimeter objective of usual type.
Fig. 426. — 4-millimeter objective of usual type.
Fig. 427. — 1.9-millimeter objective of usual type.

by the eyepiece. These tables of initial magnification will be found to vary in different catalogues even though objectives are of the same focal length, this being due to the different systems of calculating magnification. It will be found, however, that for the same focus of objective, the same focus of eyepiece, and the same tube length, the figures nearly agree. Some makers use a number system for both eyepieces and objectives, but in making comparisons only focal lengths should be considered.

In the large inverted forms of metallurgical microscopes the distance between objective and eyepiece is usually about 40 millimeters longer than in the ordinary table microscope, and therefore the magnification is increased some 25 per cent even with the same focus of objective and eyepiece; hence the difference in magnification tables for this microscope. With the many variable factors in different outfits it is difficult to make comparisons, and it is best to calculate the magnification for the particular outfit being used, especially as regards camera magnifications. To obtain the exact magnification at the ground glass of the camera, and therefore of the photograph, it is best to project a stage micrometer upon the ground glass and measure its magnified image. Micrometers graduated upon metal may be obtained for this purpose. The rulings are in tenths and hundredths of a millimeter. They are placed upon the stage and illuminated the same as a metal specimen. After focusing upon the ground glass the magnification can be measured directly without further calculation.

The aperture or numerical aperture (N. A.) is a property to which many buyers of microscopes probably pay little attention, but it is nevertheless an important

quality of an objective. The diagram in Figure 428 is shown in an attempt to simplify the theory of numerical aperture. If we assume that few, if any, objects are perfectly smooth, then light is dispersed from every point on the surface of an object in all directions up to 180 degrees. Only an extremely narrow pencil of this can be received by the unaided eye. The apparent problem of practical optics is to be able by means of lenses to gather and bring to a focus as many of the unadmitted rays as possible. In early investigation it was found that the objective which gathered in the greatest angle of rays gave the greatest resolving power.

If only dry objectives were to be considered, we might make a comparison on the basis of angular aperture, that is the angle of the cone of light which is admitted to the front lens of the objective and reaches the eye. This is important, as internal

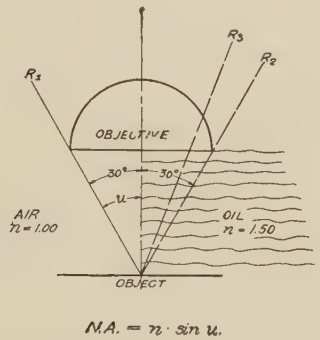


Fig. 428. — Diagram showing theory of numerical aperature.

diaphragms reduce apertures, but these apertures may be measured readily by special instruments.

A thorough study by Professor Abbe, however, proved that the only exact method for comparison of objective apertures was by comparison of the sines of the extreme admitted radiant pencils, and when the media differed between the object and the objective, the refractive indices of those media, which are 1.00 for air, 1.33 for water, and 1.50 for cedar oil. It is very evident that rays emanating from an object and passing to the objective will travel in a different angle according to the medium through which they pass, owing to the different refractive indices or bending powers of such media.

In Figure 428 is shown a ray R_1 leaving the object at an angle of 30 degrees, passing through air and just entering the extreme edge of the front lens of the objective. A second ray R_2 leaving the object at the same angle and passing through oil will be bent so as to fall within the edge of the objective lens, as shown by R_3. It is obvious that a ray leaving the object at a still greater angle than R_2 and passing through oil will be bent so as to pass into the objective. Thus a wider angle of rays is collected in case of the oil-immersion objective than in the dry objective.

It will be seen that angular aperture would not be a comparative measure for the two kinds of media. Abbe found that a value could be expressed for the different conditions by taking the sine of one-half of the angle of aperture and multiplying it by the refractive index of the media between object and objective; hence the formula:

$$\text{Numerical aperture (N. A.)} = n \sin u$$

where n = refractive index of media: air 1.00, water 1.33, oil 1.50,
and u = one-half of angular aperture.
Thus the numerical aperture on the air side would be

$$1.00 \times \text{sine } 30° = 1.00 \times .5 = 0.50,$$

and on the oil side

$$1.50 \times \text{sine } 30° = 1.50 \times .5 = 0.75.$$

This gives a method of comparison between dry- and oil-immersion objectives. The resolving power, which is the property by which an objective shows distinctly separated two small elements in the structure of an object, is directly proportional to the numerical aperture; thus an objective of 0.50 numerical aperture, as in the 8 millimeter, has twice the resolving power of the 16 millimeter, or 0.25 numerical aperture.

If a very narrow central pencil is used for illumination, the finest detail that can be shown by the microscope, with high enough magnification, is equal to $\frac{\lambda}{\text{N. A.}}$ where lambda is the wave length of the light used for illumination, say one-half micron. The wider the pencil used for illumination, the greater the resolving power until a maximum is reached, when the width of the pencil is sufficient to fill the whole aperture of the objective. In this case the resolving power is twice as great, the finest detail that the objective can show being now equal to $\frac{\lambda}{2 \times \text{N. A.}}$. For an 0.50 objective the first would be one micron with reduced aperture, and the second one-half micron with full aperture.

For practical purposes we may take the rule that the numerical aperture multiplied by 100,000 will give the number of lines per inch which can be resolved theoretically by a given objective. Thus, pearlite of say 25,000 laminations per inch should be easily resolved with an 8 millimeter objective of 0.50 numerical aperture, and a suitable eyepiece and bellows draw can be used to magnify the image to the size desired, say 400 diameters. On the other hand, an objective of say 0.25 numerical aperture could scarcely be expected to resolve this structure no matter how high we magnify the image by eyepieces or bellows extension. The magnification should never exceed 1000 times the numerical aperture; preferably it should be somewhat less, dependent upon the quality of the objective.

Depth of focus (known also as depth of sharpness or penetration) is another important factor which is often not clearly understood. It depends on the numerical aperture and the magnification, and is inversely proportional to both. The formula used to express depth of focus is $\frac{1}{\text{N. A.}}$; therefore, the higher the numerical aperture and the higher the magnification, the less the depth of focus. It is beyond the power of the optician to change these conditions. Every effort aiming at an increase of the depth of focus, for instance, by inserting diaphragms above the back lens of the objective, must necessarily decrease the effective diameter of the back lens and thus decrease the numerical aperture, thereby lowering the efficiency of the objective as regards resolving power. It may be advisable at times to introduce such diaphragming for the work to be done, and it will be shown later how such a change can be made by proper use of the illuminating system. However, objectives that show greater depth of focus than others of the same numerical aperture are not well corrected for other qualities.

The illuminating power of an objective is equal to the square of the numerical aperture, and objectives can be so compared; that is, a lens of 0.25 numerical aperture has an illuminating power of 0.062, while one of 0.50 numerical aperture has 0.25 or 4 times as great, provided it is used at the same magnification. "Flatness of field as such," said the late Dr. Carpenter, "is an optical impossibility." But by using compensation or hyperplane eyepieces to correct the margin of field, better effects are obtained, and by increasing the depth of focus by reducing the used aperture, apparent flatness is secured but at the expense of resolving power, as stated before. As an illustration of this we refer again to the statement concerning the depth of focus, which is equal to $\frac{1}{\text{N. A.}}$, hence, for an objective of 0.50 numerical aperture, the depth would be 2, while for an objective of 0.85 numerical aperture, the depth would be 1.17.

As depth of focus also varies with the magnification, if we use the above lenses at the same magnification we should naturally have greater depth in the objective

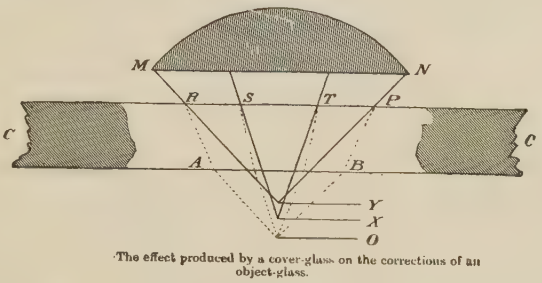


Fig. 429. — Effect of cover-glass upon focus.

of 0.50 numerical aperture, and if this gives sufficient resolving power for the work in hand it may be used to obtain a flatter field.

Defining power depends upon the finest correction of spherical aberration and chromatic aberration, the perfect centering of the lenses of the objective, and in fact on the general excellence of the mechanical work involved in the making, and it is here that the optician must show his skill. It should be borne in mind that the finer the definition of an objective, the more sensitive it is to incorrect focusing and to slight changes of the adjustment through vibration, etc. In constructing objectives their formulæ should be based upon rigorous computations, all elements of construction, such as glass, radii, thickness of lenses, separation, etc., being determined in advance wholly without recourse to experiment. This method of construction is the only one insuring uniformity in optical systems of such intricacy as a microscope objective.

It will be well to consider at this time the effect of tube length, that is the distance between objective and the eyepiece with which it is used. Most of the objectives used on biological and smaller metallurgical microscopes are corrected for a mechanical tube length of 160 to 170 millimeters. By mechanical tube length is meant the distance from the shoulder against which the objective screws to the shoulder against which the eyepiece rests. In the case of the larger metallurgical stands of the inverted type this distance is usually longer, owing to reflections necessary to secure an inverted stage and a convenient position for the viewing tube. Therefore, the objectives used on this type of microscope should be corrected for this extra length.

The use of objectives at incorrect tube length, especially in powers over 100 diameters, will result in inferior definition. This is especially true in metallographic work.

Objectives for metallurgical work must also be corrected for use without cover-glass, as specimens of metal are examined without covering.

All objectives used in biological microscopes are corrected for the refraction which takes place when the ray from the object passes through a thin piece of glass. These objectives are not suited for use on uncovered objects, and if used in metallurgical work only inferior results will be obtained except with the very lowest powers, such as 16 millimeters or lower. To show the effect of cover-glass, Figure 429 has been taken from Carpenter's book on the microscope. It will be seen that without the cover-glass, an ordinary microscope objective would focus at different planes for the

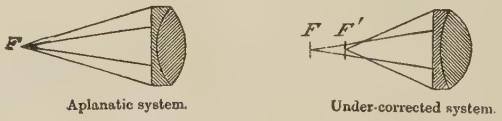


Fig. 430. — Under corrected system obtained without use of cover-glass.

central and marginal zones, as shown at points y and x, but with the refraction of the cover-glass the rays all focus at the point o.

Therefore if the ordinary objective is used without cover-glass, it will work as an under-corrected system, as shown in Figure 430, whereas when corrected for use without cover the objective should be perfectly aplanatic, as shown at the left, all rays focusing at one point. This correction cannot always be accomplished by changing distances between lenses but requires special computation. The oil-immersion objective, however, needs no special correction as regards cover-glass, because the immersion oil and cover-glass are of the same refractive index, and if the cover is missing, the additional strata is made up by a thicker layer of oil. The tube length, however, must be correct even in this case.

As to the objective mounts, both long and short mounts are used in metallurgical work. The short mounts should always be used with mirror or prism illuminators so as to bring the illuminator as near to the back focus of the objective as possible. The tendency of late, however, has been to use short mounts for all kinds of illuminators.

The objectives previously described are of the achromatic type, but the same characteristics are also found in the apochromatic objectives, and they are even more sensitive to deviations from the standards for which they are made. The usual focal lengths and numerical apertures are as follows:

Focal Length	Numerical Aperture (N.A.)	
	apochromatic	achromatic
16 millimeters	0.30	0.25
8 "	0.65	0.50
4 "	0.95	0.85
3 "	0.95	0.85
2 "	1.30	1.25

It will be seen that the numerical apertures are somewhat greater in the apochromatic objective. This means increased resolving power and other features attending higher aperture. These lenses have other improvements than increased aperture.

The word apochromatic means free of color and is illustrated by Figure 431. If we were to form an image with an ordinary lens of non-achromatic form, a ray of white light coming from the object would be broken up into the several colors of the spectrum and images would be formed at different distances from the lens corresponding to each color. There would thus be a series of images, one behind the other, ranging from violet to red, the shorter waves being refracted more than the longer ones.

In the standard achromatic objective, two of these colored images would be combined, and in apochromatic objectives three colored images would form in the same

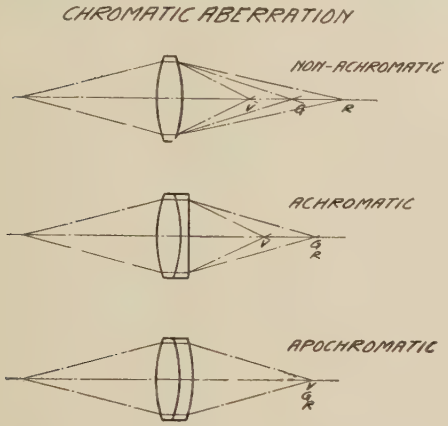


Fig. 431. — Illustration of apochromatic lens.

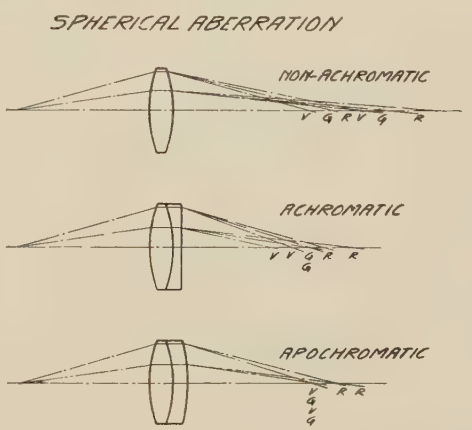


Fig. 432. — Correction for spherical aberration.

plane, and as the violet rays are brought to a focus at the same plane as the apple-green visual rays, these objectives are excellent for photographic purposes, even when used without filters. As shown by Figure 432, the correction for spherical aberration is more perfect. Spherical aberration refers to the fact that in an ordinary uncorrected lens the portion of a ray coming through the center and the portion coming through the outer zones are focused at different planes. In the uncorrected lens this applies to all colors; in the achromatic objective the correction is made for one selected color, say green, and in the apochromatic for two colors. Therefore, for the very finest class of investigations the apochromatic objectives are essential owing to their finer color and spherical corrections. These corrections are accomplished by the use of special glasses and a transparent substance known as fluorite. Another series of objectives now offered upon the market is the 4 millimeter dry and 1.9 millimeter oil immersions, known as semi-apochromatic objectives. They have one fluorite element and are much better than the regular achromatic objectives. They make a good compromise where cost will not permit the purchase of apochromatics.

EYEPIECES

The second part of the optical equipment to be considered is the eyepiece, so called because it is used near the eye. This may, however, lead to some confusion, as the eyepiece is also necessary when forming the image upon the ground glass of the camera. Some users of this class of apparatus have been found who thought the eyepiece was needed only in visual work. Small photographic lenses are used without eyepieces, as later explained. The ordinary eyepiece shown in Figure 433

is known as the Huygenian form, after its designer. It consists of the two non-achromatic plano-convex lenses with a diaphragm for limiting the field between them. The upper lens is known as the eye lens and the lower as the field lens. Huygenian eyepieces are made in a variety of powers, as 5 X, 6.4 X, 7.5 X, 10 X, and 12.5 X, these designations meaning that they magnify the image formed by the objective by these amounts. Different makers used different designations for their eyepieces and this is liable to cause confusion if attempt is made at comparison.

In the case of Leitz and Zeiss the eyepieces are numbered from 0 to 5, but the

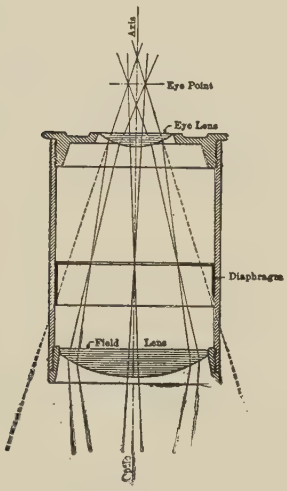
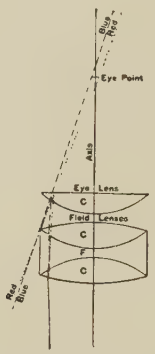


Fig. 433. — Eyepiece of Huygenian form.



Positive Compensation Ocular.
(From Spitta, p. 110).

Fig. 434. — Compensation type eyepiece.

eyepieces of the Bausch & Lomb Optical Company are marked with their magnifying power as 5 X, 10 X, etc.

A new eyepiece known as the hyperplane produces a flatter image plane than the Huygenian eyepiece and allows for a larger field of view, well adapted for photomicrography. These eyepieces have a compensation about half-way between the Huygenian and compensation eyepieces described below.

The hyperplane eyepieces are made in powers from 5 X to 20 X and may be used with all classes of objectives.

Another form of eyepiece is known as the compensation eyepiece, shown in Figure 434, so called because it compensates for the variation in size of the blue and red images given by the apochromatic objective. While the apochromatic objective is so constructed as to bring these colors in focus at the same plane as previously stated, the images formed are not of the same size, and this is neutralized by the compensation eyepiece. They should, therefore, always be used when one is using apochromatic objectives, and they may be used to good advantage with the high-power achromatic objectives. The compensation eyepieces of various makers are not always interchangeable with different apochromatic objectives.

These eyepieces vary in construction and in the number of lenses according to their power. They are made in powers from 5 X to 25 X, much higher than the Huygenian type, and it is possible to use these high powers with the apochromatic objectives owing to their finer color correction.

There is another type of eyepiece known as the projection eyepiece, in which the eye lens or lens nearer to the photographic plate is adjustable according to the bellows extension of the camera. With this adjustment one is able to use the objective in the same relative position to the object as it is when used for visual work. Some of these eyepieces have a very small opening in the diaphragm, which is liable to indicate that the field is unusually flat.

It is possible to get similar effects as those produced by the projection eyepieces with ordinary eyepieces by partially withdrawing them from the eyepiece tube when making photographs. This distance may be found by the formula:

$$\frac{\text{square of eyepiece focus}}{\text{length of camera draw}}$$

Thus for a 5 X eyepiece of 50 millimeter focus and a bellows draw of 250 millimeters, the eyepiece would have to be extended 10 millimeters, or it may be determined by experiment. It will be seen that the distance becomes greater with low-power eyepieces and short bellows draw. This adjustment keeps the objective in the same relation to the object as when used in visual work, as previously stated, and preserves its best spherical correction, tending to flatten the fields.

Too much stress cannot be laid upon the necessity of keeping all of the optical parts clean and free from dust, grease, or finger marks. Poor results are often due to this neglect.

VERTICAL ILLUMINATOR

In Carpenter's book on the microscope it is stated that the first vertical illuminator was made and used by Prof. H. L. Smith of Geneva, N. Y. Smith's illuminator consisted of a piece of speculum metal so placed as to reflect light down through one side of the objective, the image returning through the opposite side. The plane-glass illuminator is said to have been designed by Beck of England. In this form the light is reflected by the surface of the glass through the objective and the image returns from the specimen through the glass to the eyepiece. Formerly much flare was experienced in using this type of illuminator, but it can be eliminated by proper illuminating appliances and diaphragms. Both forms of illuminator are in use today, the first in the form of mirrors and prisms and the latter much in its original form.

The mirror and prism types are preferred by some workers, and while they are satisfactory for low powers and relief work, they reduce the available aperture of the objective by nearly one-half with consequent reduction in resolving power. They do give increased illumination, due to total reflection, and may be used for projecting metal specimens with low powers when several observers wish to study the image. For high powers and utmost resolution, the plane-glass reflector is best.

Vertical illuminators have appeared from time to time in many forms. The one shown in Figure 435 is a base model to which can be fitted mirrors, reflector, plane-glass reflector, lenses and diaphragms, as desired. For visual work, side tubes with lenses and lamps may be attached and used successfully, but when high-power illumination is used and the beam of light must be carefully centered to the objective, the best results can be obtained by having condensers and lamps on separate standards. A recent addition to this type of illuminator consists in clamping screws, whereby all adjustments can be locked so that once adjusted the illuminator cannot be

deranged easily. Care must be exercised to keep the glasses of the illuminator clean and to prevent distortion by bending the mount when cleaning, as it will tend to destroy the definition.

Figure 436 shows a condenser and iris diaphragm mounted on a separate standard in place of mounting it integral with the vertical illuminator. This is termed by the

Fig. 435. — Vertical illuminator to which can be fitted mirrors, reflector, plane glass reflector, lenses, and diaphragms as desired.
Fig. 436. — Condenser and iris diaphragm mounted on a separate standard.

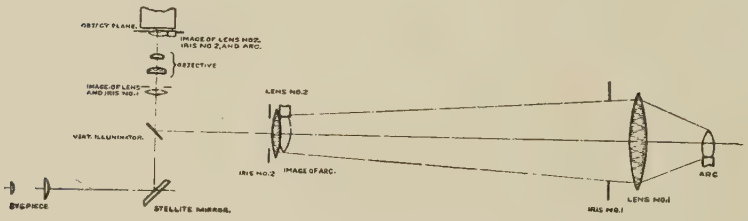


Fig. 437. — Method of obtaining critical illumination.

makers a supplementary condenser, to distinguish it from the condenser at the arc lamp. Its use and adjustment will be explained later.

Critical Illumination. — It is generally agreed by expert microscopists that the best results are obtained when the specimen is examined or photographed with critical illumination. Critical illumination is obtained when the image of the illuminant and specimen are about in one plane, also when removing the eyepiece and examining the back lens of objective through a pinhole cap, it is possible entirely to fill the lens with light. In Figure 437 is shown how this kind of illumination may be obtained. The arc or Pointolite illuminant is nearly imaged on the supplementary condenser No. 2 by the aspheric condenser No. 1 with a distance of about 25 to 30 inches between the two lenses. This should give an image of the illuminant of about 25 to 30 millimeters diameter. The image should be slightly ahead of the supplementary lens No. 2 if an arc is used so as to avoid imaging gas bubbles upon the specimen.

An image of the fully and evenly illuminated aspheric lens No. 1, and its iris diaphragm, referred to later, are projected into the back focus of the objective by means of the supplementary condenser No. 2 and the vertical illuminator. The supplementary lens is of such focus and set at such distance from the objective, that is the same optical distance as the eyepiece diaphragm from objective, that the image of the arc, the evenly illuminated lens No. 2 and its iris, are imaged by the objective upon the specimen when the objective is at proper focus. By closing the iris in front of the aspheric condenser, the aperture of the light cone entering the objective is reduced similarly to that accomplished on some outfits by placing an iris diaphragm on the side of the vertical illuminator but in a better location, as it is in the back focus of the objective. This reduction of the light cone below the aperture of the objective

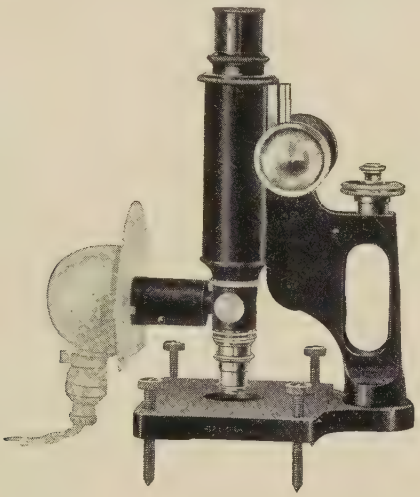


Fig. 438. — Tassin microscope with illuminating device attached to vertical illuminator.

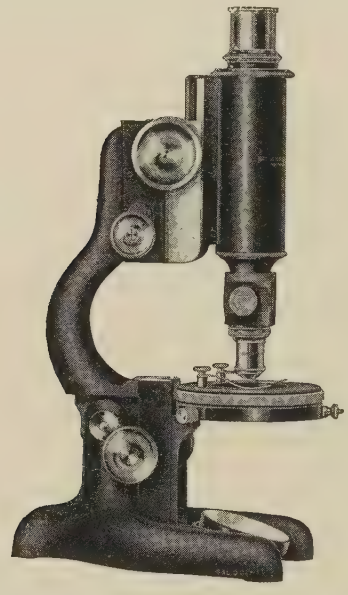
gives decreased illumination, and decreases the numerical aperture with attending results; for example, less resolving power, greater depth of focus, and greater flatness. Full apertures are obtained with iris opening of 16 millimeters for 4 millimeter objectives, and 18 millimeters for 16 and 32 millimeter objectives.

The iris of the supplementary lens No. 2 being imaged on the specimen, when closed, reduces the size of the illuminated spot upon the specimen, reducing the visible field. By just opening this diaphragm enough to clear the field of view, unnecessary rays are cut off, which rays if they fall on tubes of the objective, illuminator, etc., might cause a flare. The light returning from the specimen after passing through the objective and vertical illuminator, is reflected by a stellite mirror to the eyepiece. The use of a metal mirror reduces all chance of flare which might come from the plane surface of a glass prism.

With the appliances just mentioned, the illumination scheme for metallurgical work as described in the Zeiss circular, Micro No. 89, may be obtained, although the adjustments are somewhat different. It should be noted that in both visual and photographic work, decrease in illumination should be accomplished by filters and not by diaphragms which reduce aperture, unless reduction of aperture is desired to secure certain results. It will be shown later how these optical parts are adjusted to secure the best results as regards centering.

MICROSCOPES

Any ordinary microscope with proper optics may be used in the examination of metals, but it is in this case either necessary to mount each and every specimen at a fixed height to avoid readjustment of the illumination or to have an illuminating device attached to the vertical illuminator, as shown in Figure 438. This stand is somewhat like the workshop microscopes of Swift and Watson, after the design of Mr. Stead. The illuminating device consists of a 6-volt incandescent lamp, operating on the regular 110-volt circuit, and two condensers. As can be seen from the illustration, it is attached to the illuminator and moves with it and the optical parts. It may be applied to any ordinary microscope, and the results obtained are good



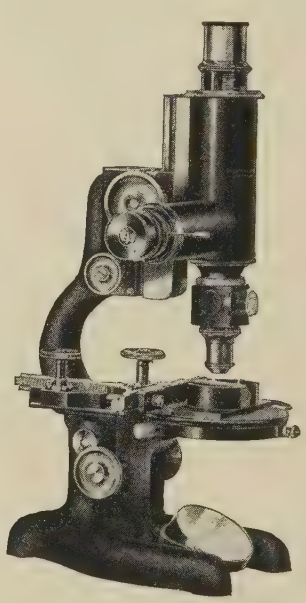


Fig. 439. — Typical metallurgical microscope with delicate adjustment and a revolving stage with centering screws.
Fig. 440. — Same as Fig. 439, with a mechanical stage attached.

for magnifications up to about 200 diameters in visual work. It may also be used in photography for about 100 magnifications, but of course cannot compare with the better instruments and cameras.

The general form of stand for metallurgical work, however, is one in which the stage and specimen are movable by rack and pinion, as by this method varying thicknesses of specimen can be accommodated without deranging the illuminating system. Instruments of this type require the mounting of the specimen in wax or other form of holder. In the case of steel specimens a Sauveur magnetic holder may be used, the specimen being held from the under side by magnetism.

Figure 439 shows a typical form of metallurgical microscope to which a mechanical stage may be attached if desired. The stand illustrated in Figure 440 differs from the preceding model in that it has a side tube for connecting to the camera, so that visual observations can be made without disconnecting or moving the camera, the only operation necessary being the withdrawal of the side tube, with its prism, from the optical axis when making visual observation or in adjusting the light and the specimen.

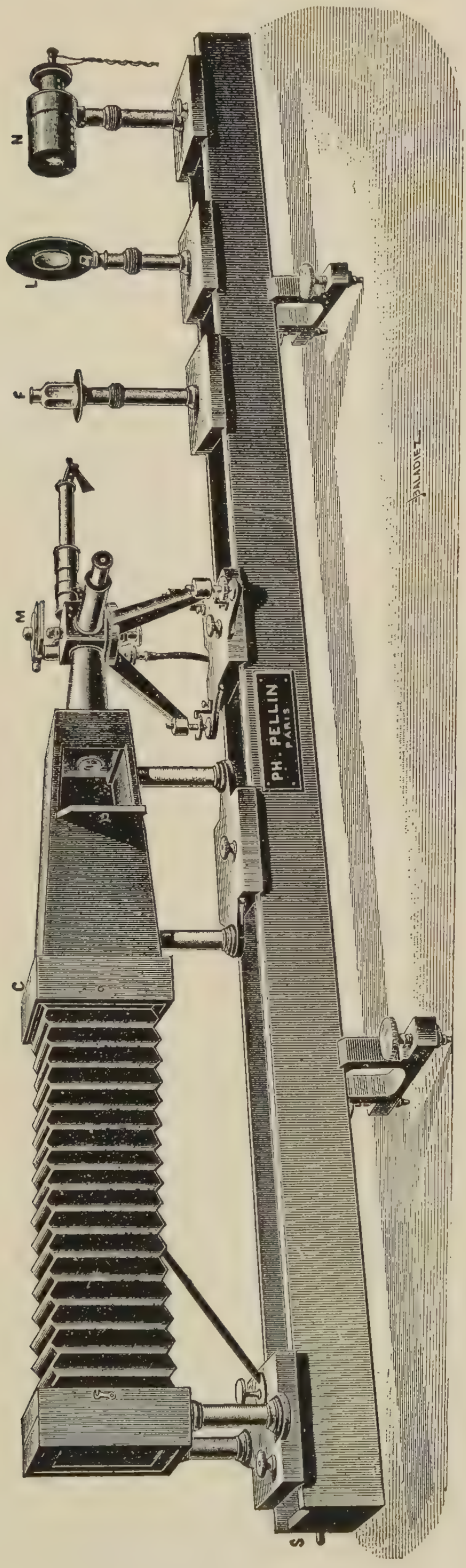


Fig. 441. — Le Chatelier inverted metallurgical microscope. Ph. Pellin.

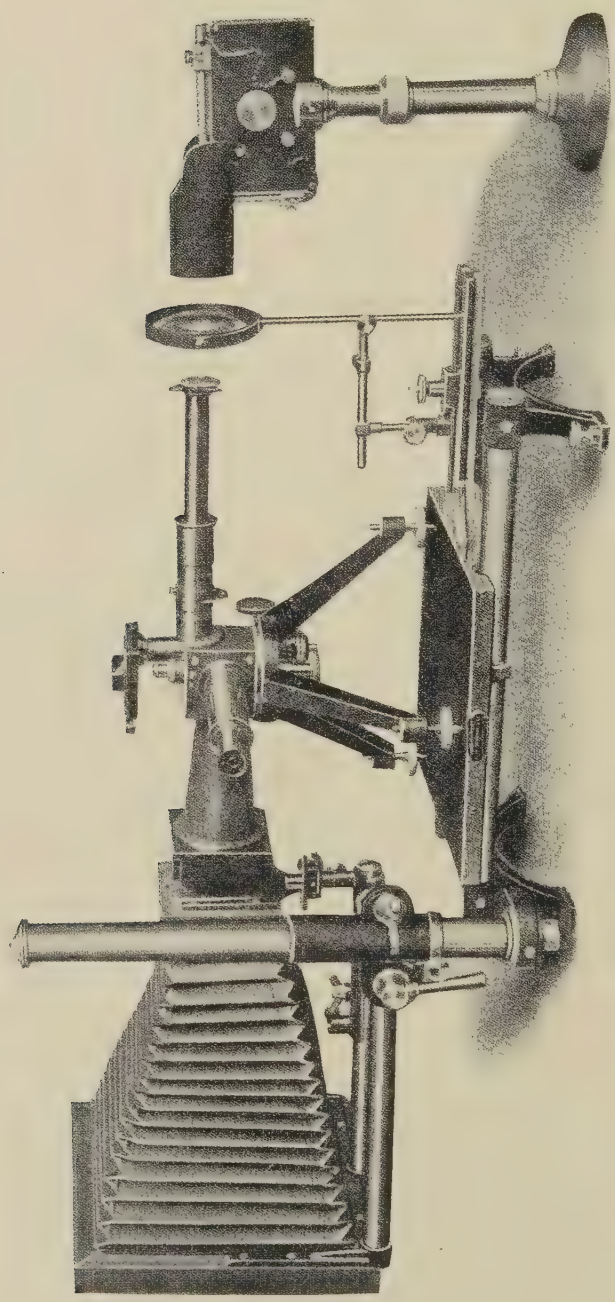


Fig. 442. — Inverted metallurgical microscope. P. F. Dujardin & Co.

Many workers prefer a stand of the inverted type, that is one in which the stage is above instead of below the objective, and in which it is necessary to prepare one surface only, the polished face being placed face down upon the stage over the objective. The inverted form of microscope is credited to Le Chatelier in the year 1897.

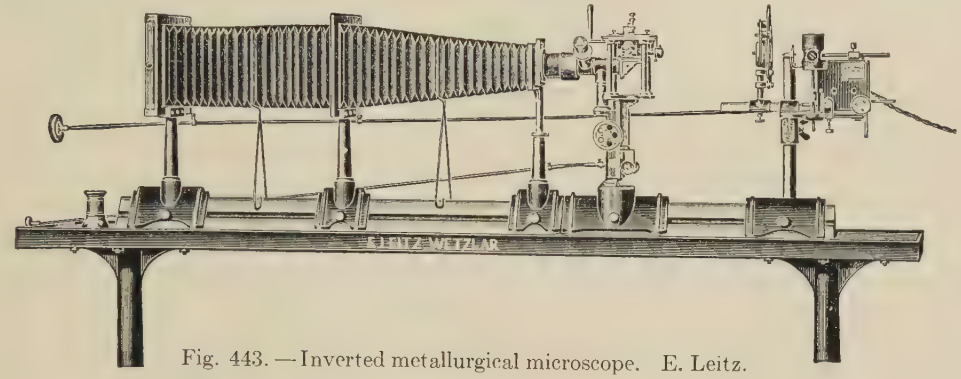


Fig. 443. — Inverted metallurgical microscope. E. Leitz.

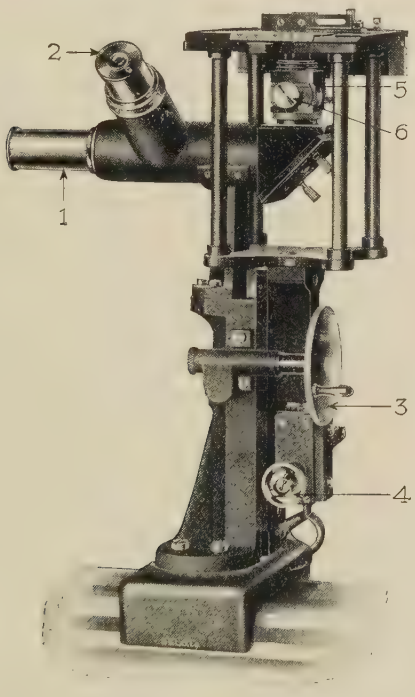


Fig. 444. — Close view of microscope and plane glass with vertical illuminator set at 45 degrees.

It has been made in a variety of forms, first by Pellin of Paris (Fig. 441), later by Dujardin & Co. (Fig. 442). Other models have been made by Leitz (Fig. 443) of Germany and Reichert of Austria.

Figure 444 shows the large inverted stand of the Bausch & Lomb Optical Company, and embodies all the desirable features of a metallurgical microscope. In this model

all parts are of heavy construction and the pieces are limited to the least number to insure rigidity. The rack and pinion is massive and the fine adjustment is of the side-lever type, which automatically compensates for wear. Both adjustments, the rack and pinion and the fine adjustment, move the stage and specimen, the optical parts, including the vertical illuminator, being fixed at all times, and when once centered, no change occurs during focusing. The reflector below the vertical illu-

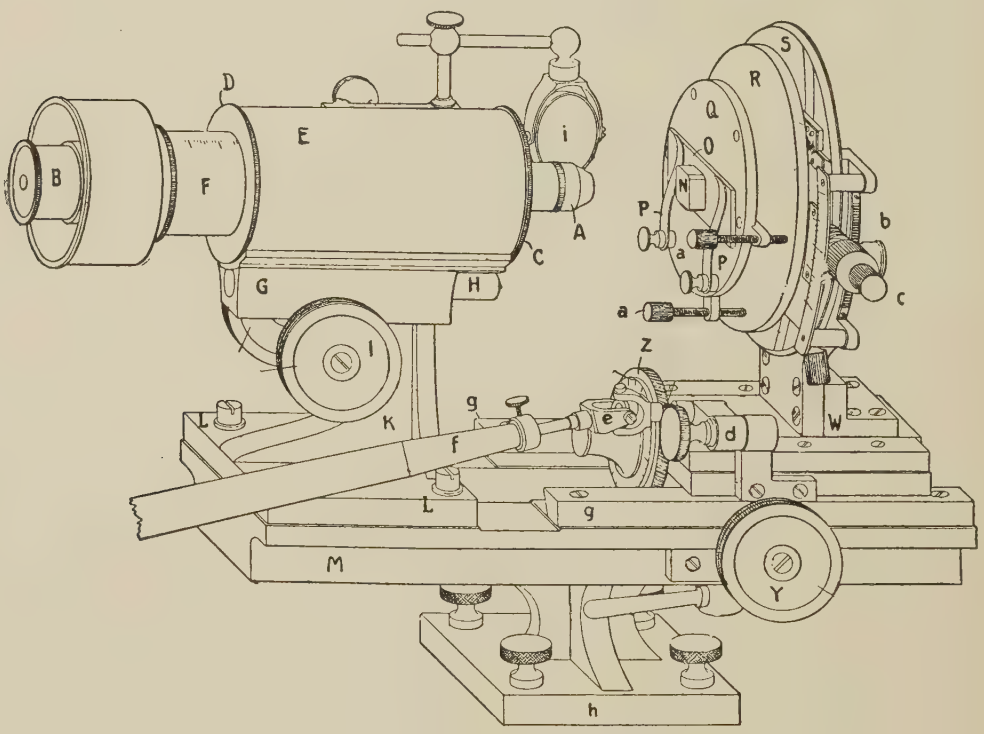


Fig. 445. — Marten's metallurgical microscope. (Zeiss.)

minator is of stellite, a hard non-corrosive metal. The mechanical stage has all adjustments from below, and clamps are provided for holding small specimens and thin sheets of metal under observation.

Other types of metallurgical microscopes which should be mentioned are those of Martens, made by Zeiss (Fig. 445), and the Rosenhain microscope, made by Beck (Fig. 446). The Martens' stand is of horizontal type, provided with movable stage, and is in general form similar to the stands first described. The specimen must be mounted so as to retain the polished surface in a vertical position. The illuminating apparatus is placed at right angles to the axis of the microscope. The Rosenhain is an enlarged and heavy form of usual type and has its vertical illuminator built into the tube.

ILLUMINANTS

The direct current arc of low amperage is no doubt the best illuminant to use if intensity is desired. The lamp may be of the hand-feed variety, but it is better to use a lamp having an automatic mechanism for feeding the carbons. Figure 447 shows a lamp of hand-feed type, and Figure 448 shows the automatic feed type,

both lamps interchanging on the same standard. Suitable condensers must be used to collect a wide angle of the beam emitted from the lamp and condense it into the vertical illuminator. Centering screws are usually provided so that the illuminant can be well centered to the condensing lenses.

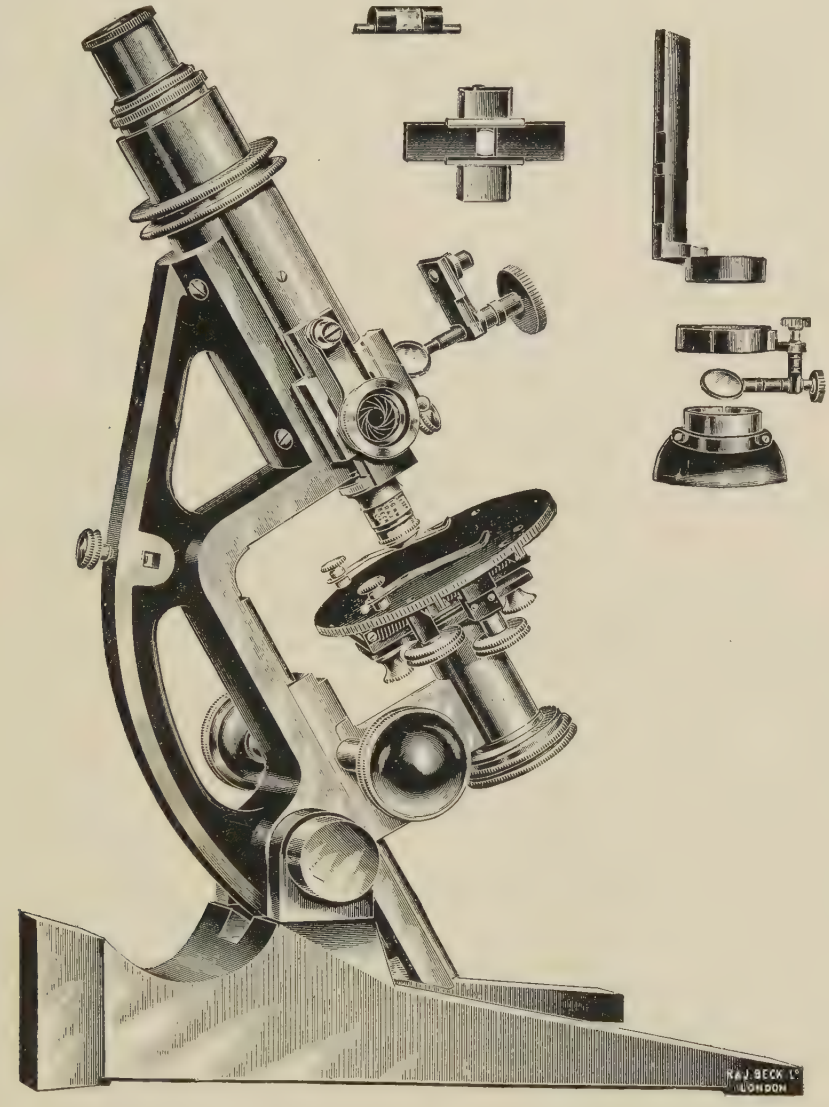


Fig. 446. — Rosenhain metallurgical microscope. R. and J. Beck.

The carbons used on direct current for 4 to 5 amperes are usually 8 millimeters diameter for the positive or horizontal carbon and 6 millimeters for the negative. It is necessary to see that the positive wire of the electric current is on the horizontal carbon. This can be determined by noting the brightness of the carbons through the smoked-glass window, the brighter one being the positive.

For alternating current the carbons should be 7 millimeters diameter for both horizontal and vertical, and it makes no difference how the wires are connected.

For visual observation and for photography where speed is not essential, a Mazda lamp with ribbon form of filament makes a very acceptable illuminant. It has the advantage of giving a constant and uniform illumination and requiring no care when

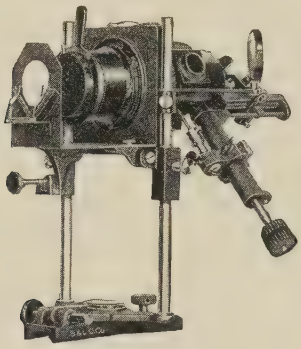


Fig. 447. — Arc lamp, hand feed type.

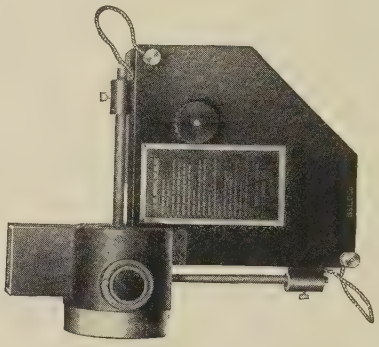


Fig. 448. — Arc lamp, automatic feed type.

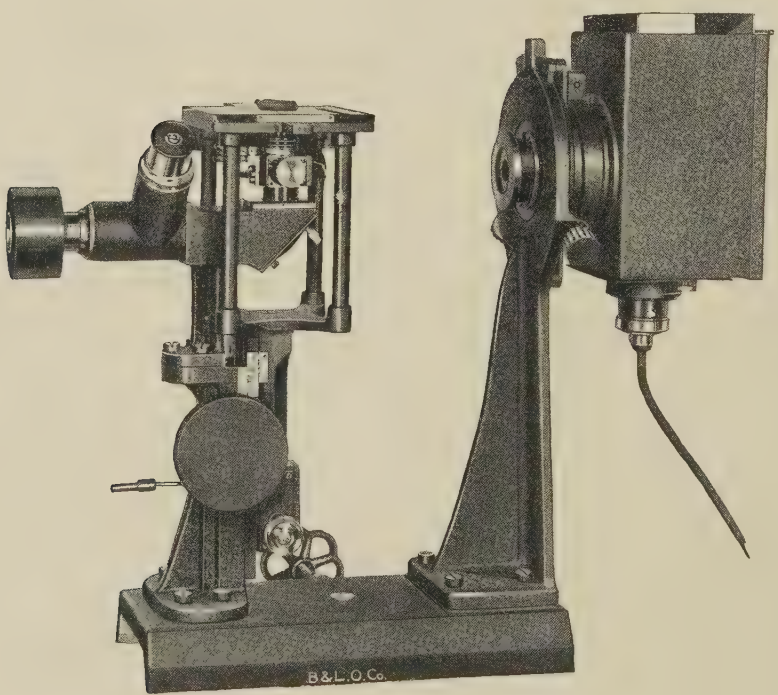


Fig. 449. — Inverted microscope and illuminating device.

once adjusted. This lamp, however, uses only 6 volts and is best used with an alternating-current supply in connection with a transformer, as the amperage rating is 18.

The outfit (Fig. 449) combining the microscope and illuminating device is of recent design. The microscope proper is of particularly substantial construction throughout. The vertical column supporting the optical tube and the stage is of unusually large cross-section, and broad bearing surfaces are provided especially

for the coarse adjustment which moves the stage upward or downward with reference to the fixed objective.

A new feature of this instrument is the graduated scale on the rack slide, by means of which one can quickly set the stage for different objectives, so that the object will be approximately in focus so that final focusing can easily be accomplished by means of the fine adjustment only.

The stage of the microscope is provided with rack and pinion movement in two directions, and is provided with a circular stage plate which has a V-shaped slot in it for accommodating specimens of various sizes and shapes.

The vertical illuminator (Fig. 450) is fitted with a sliding plate by means of which it may be removed from the microscope if desired, although it is centered

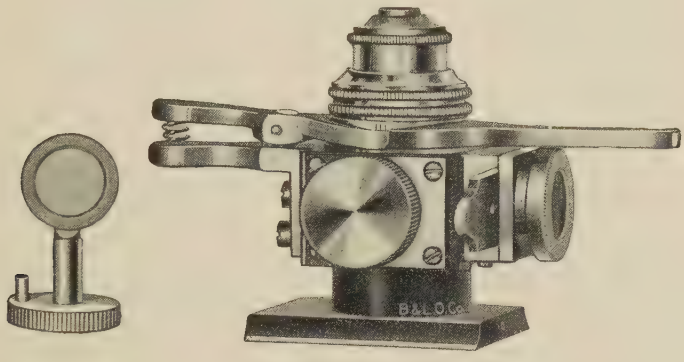


Fig. 450. — Vertical illuminator with sliding plate.

with reference to rotation about its vertical axis and locked in position. A stop is also adjusted to assure one that the clear-glass reflector is at exactly 45 degrees to the axis of the objective. For those desiring greater illumination, or oblique illumination with lower power, a semicircular mirror is supplied to interchange with the clear-glass reflector. The opening of the side of the vertical illuminator is fitted with a short tube in which is mounted a small condensing lens, a sliding diaphragm with four apertures and two solid-glass filters, which produce approximately monochromatic light equivalent to the E-line of the mercury spectrum, which is the wave length for which the achromatic objectives are corrected and which we have found to be the most satisfactory for general metallographic work, particularly for iron and steel.

The full numerical aperture of the objective may be used, or the aperture may be reduced by selection of the opening in the sliding diaphragm. The maximum resolution with any objective will be obtained when the largest-sized aperture is used. The flatness of the field can be increased, with a sacrifice of resolution, by using the smaller openings in the sliding diaphragm.

The top of the vertical illuminator is provided with a quick-changing holder or clutch to facilitate the interchange of objectives.

The illuminating unit shown in Figure 449, consisting of the condensing or collective-lens system and the light source, is supported upon a very substantial standard, permanently attached to the base upon which the microscope is also mounted. The condensing system is composed of three elements of approximately 1½-inch diameter and of short focus so that the illuminating unit may be brought close to the micro-

scope. The lenses are mounted in a sliding tube for focusing, and the front of the mount is provided with an iris diaphragm, which may also be used for controlling the size of the beam of light.

The axis of this condensing system is permanently centered with the center of the supplementary condenser on the side of the vertical illuminator so that the only adjustment that is necessary by the user in aligning the illuminating system is to

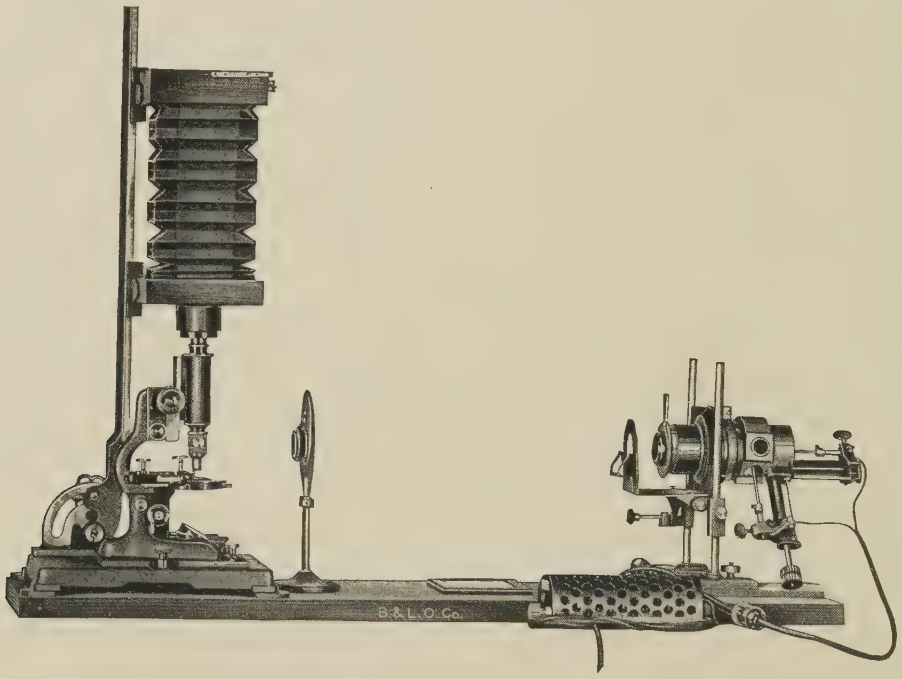


Fig. 451. — Simple type of vertical camera.

bring the light source into alignment with the axis of the condensing system, — a very easy adjustment by means of two centering screws.

The light source may be either a ribbon-filament Mazda lamp or an automatic arc lamp, as both are supplied in housings which are readily interchangeable on the illuminating unit support.

Cameras. — The cameras and supports available for this work probably are as great in variety as the microscopes. A few types will be referred to, all of which embody supports to carry an illumination system of the type described. Figure 451 shows a simple type of vertical camera which has been in use for a number of years. It differs from the ordinary, in that the camera and all accessories are mounted on a single base board to which they can be clamped after adjustment. It is annoying in this work to have a number of loose parts which are readily disturbed. Figure 452 shows a low form of stand with vertical camera. When resting on the floor the ground glass is at a convenient height for observation. The camera may be swung to one side when making adjustments of the specimen and illumination.

Figure 453 shows a type especially designed, after suggestions of Professor Sauveur, for use with the side-tube microscope. As stated, when referring to the microscope, the side tube is withdrawn for visual observation and again pushed into the path

of light when making photographs. The light-tight connector between camera and microscope is so made that neither camera nor microscope need be moved in making

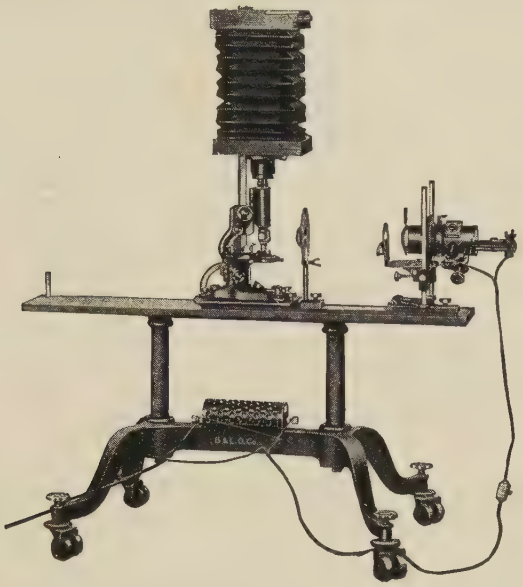


Fig. 452. — A low form of stand with vertical camera.

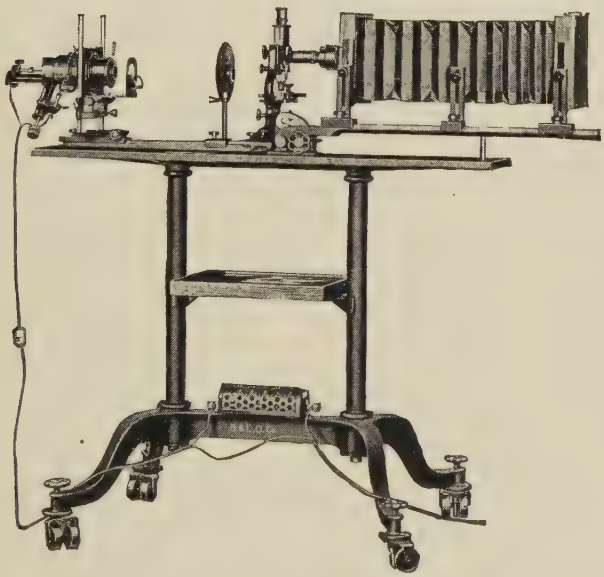


Fig. 453. — A camera especially designed for use with side-tube microscope.

the adjustment from visual to photographic use. All the camera supports described are made with either 4 by 5 or 5 by 7-inch cameras. Figure 454 shows a camera known as the GSA type, and is used with large inverted microscope IL. The camera takes all sizes of plates from 3 by 4 to 8 by 10 inches by means of kits in the plate

holders. The larger sizes are useful in gross photography with low magnifications or reductions. Devices for feeding the arc lamp and for adjusting the fine adjustment from a position behind the ground glass are supplied. The arc may also be adjusted while making visual observations, and an adjustable mirror is furnished so that the arc can be observed from all positions. This makes the use of a hand-feed arc convenient. Two focusing screens are supplied, the ground glass for giving a general view of the entire image and a clear glass for fine focusing with focusing glass. These are set at right angles to the axis of the camera, and images are formed direct and not by reflection. A plate holder of book form is supplied, and trial exposure may be made by withdrawing dark slide, giving the plate an exposure of

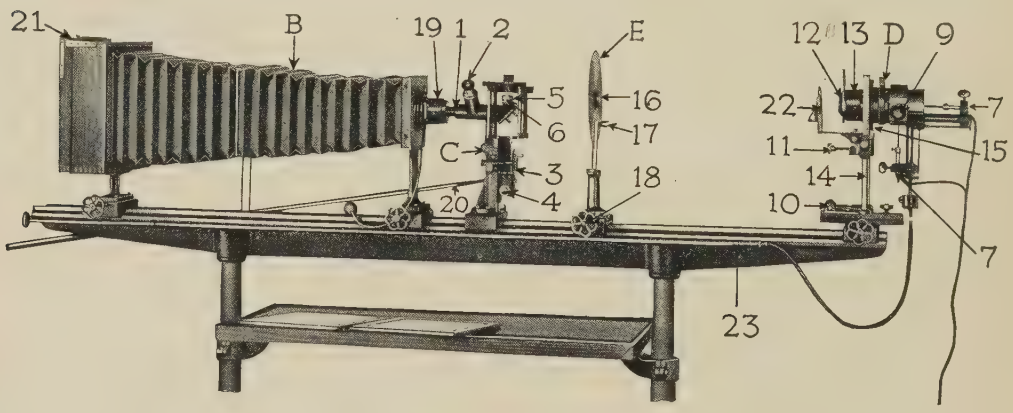


Fig. 454. — Large inverted microscope and camera.

15 seconds; replacing slide 1 inch at a time, giving each succeeding inch 15 seconds, so that the final exposure on a 5-inch plate would be 75 seconds, 60 seconds, 45 seconds, 30 seconds, and 15 seconds for the various parts.

After some experience it is easy to judge the correct exposure for a given class of objects. Special appliances are made to meet the requirements of various workers. This camera is also supplied in low form to place on a laboratory bench. In using high powers with all outfits, time must be given for all parts to settle in position, and then make final adjustment of focus. The microscope should be focused; then, after a time equal to exposure, the image should be examined. If still in focus the exposure may be made. If out of focus this operation should be repeated, the exposure postponed until all adjustments have come to rest.

Some of the difficulties in the use of metallographic equipment are due to improper adjustment, because it is often found, on examining an outfit, that it is not properly centered, or the parts are not in the proper relation to each other. As the large inverted type is now widely used, the method of adjustment will be described, although these same adjustments apply equally well to smaller outfits fitted with same devices, and instructions may be secured from the makers. One of the main points is the centering and focusing of the illuminating pencil or cone of light. If this is incorrect, good results cannot be obtained. The various parts in Figure 454 have been numbered for easy reference.

The microscope, C, should be 35 inches from the lamp, D, so as to obtain an arc image of sufficient size to cover the field, that is the area of the supplementary lens.

If this is not evenly illuminated the field of the objective will not be evenly illuminated. The center of the lamp should be on the same center as the opening of the vertical illuminator, No. 5, and the vertical rods are now graduated to show this position. For preliminary adjustment the supplementary lens should be removed from its standard, and the aspheric lens, No. 13, adjusted so as to give an arc image at a point about 26 inches from the lamp. Then one should close iris, No. 12, in

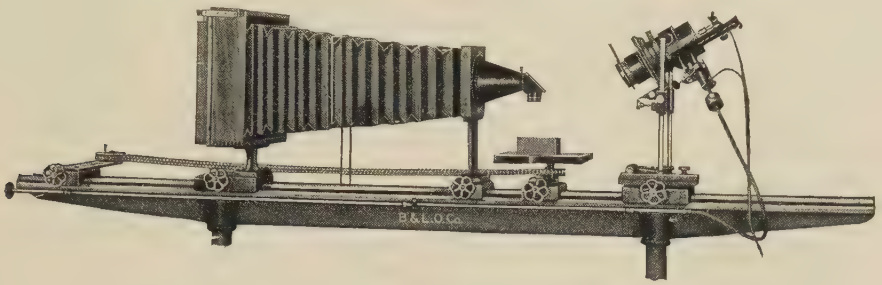


Fig. 455. — Arranged for attaching low-power photographic lenses to camera, and device for holding and focusing the specimen.

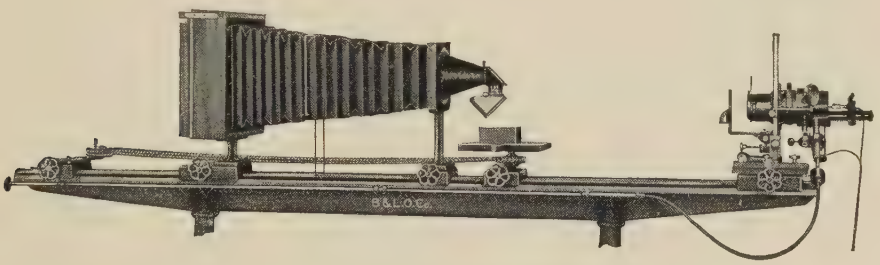


Fig. 456. — Plane glass holders supplied for vertical illumination with low-power lenses.

front of arc condenser to a small opening, say ¼ inch. It is assumed that the objective, say 16 millimeters, is in position on the vertical illuminator at No. 5.

Figure 455 shows an arrangement for attaching low-power photographic lenses, of the 32-, 48-, and 72-millimeter foci, to camera, and special device for holding and focusing the specimen. The focusing is done by chain movement from rear of camera while observing the ground glass. It is intended for the photography of fractures, etc. This also shows the illuminant as used for oblique illumination. Plane glass holders are supplied for vertical illumination with these low-power lenses, as shown in Figure 456.

The camera shown in Figure 457 is a small outfit for student use and for industrial plants where only a small amount of work at low and medium powers is required. The microscope is of the inverted type and is mounted over the camera. The specimen is examined by means of a side tube which, with its prism, may be withdrawn from the optical axis, permitting the image to fall upon the plate in the camera. While the image may be focused upon an opaque screen in the camera, it is possible so to adjust the camera eyepiece that the image is sharp upon the plate when focused for visual observation. The illuminant is the 6-volt, 108-watt Mazda lamp. The mountings for lamp and the condensers are of much simpler form than in the previous outfits, but will give satisfactory results in magnifications from 50 to 400.

Figure 444 shows the microscope closer, and the plane glass, No. 6, of the vertical illuminator set at about 45 degrees. Place a highly polished unetched specimen on stage face down, focus objective, and while observing in the eyepiece bring the small spot of light to the center of the field. The spot should appear as the one in Figure 458 marked correct. If it is off center, the vertical illuminator should be adjusted either

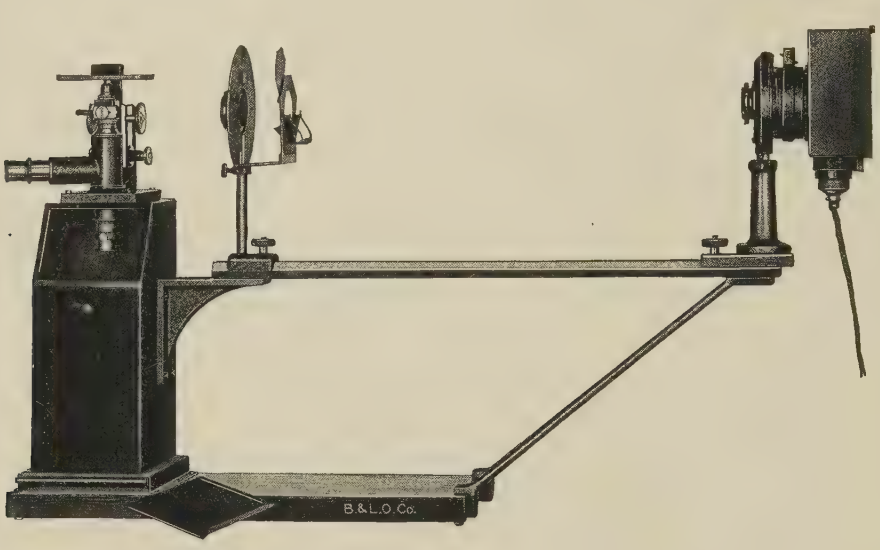


Fig. 457. — Small metallographic outfit for student use.

Fig. 558. — Method of adjusting light spot with plane glass.

by knob of plane glass, No. 6, or by rotating the illuminator upon the vertical axis until the spot is centrally located.

Going back to Figure 454, focus the objective roughly and remove eyepiece, No. 2. Place over the eyepiece tube a pinhole diaphragm, for centering the eye with tube. Place supplementary lens, E, in position about 6 inches to right of microscope, and while observing through pinhole cap, adjust this condenser until the bright spot is in center, as just shown. Then replace eyepiece and close iris, No. 16, of supplementary lens. If the iris is not sharply defined, slide the supplementary lens on its base, No. 18, to or from the microscope until the blades of iris diaphragm can be distinctly seen in the field, when objective is in focus. In making these last observations, the smoked-glass cap should be used over the eyepiece. The image of this iris should be concentric with diaphragm of the eyepiece, and will be if set-up has been correctly made.

If the arc is now focused on the supplementary lens, the light condition should be as shown in Figure 437. The arc is nearly focused on supplementary lens No. 2, by lens No. 1. Lens and iris No. 1 are focused at back of objective by lens No. 2. Arc, lens, and iris No. 2 are focused on specimen by the objective. This gives critical

illumination. When these results are obtained, good images are secured. After a little practice it is not difficult to set up the apparatus in the manner described. Some users introduce a ground glass in front of the arc. This diffuses the light, and while giving even illumination, it does not give critical illumination as previously described, but is preferred by some for lower powers and is even recommended by some workers.

In adjusting the mirror illuminator, or if a prism illuminator is used, the same conditions prevail. The spot of light is to be centered in the field as before, and the supplementary lens then placed in position and the location of the light pencil

Fig. 559. — Method of adjusting mirror illuminator.

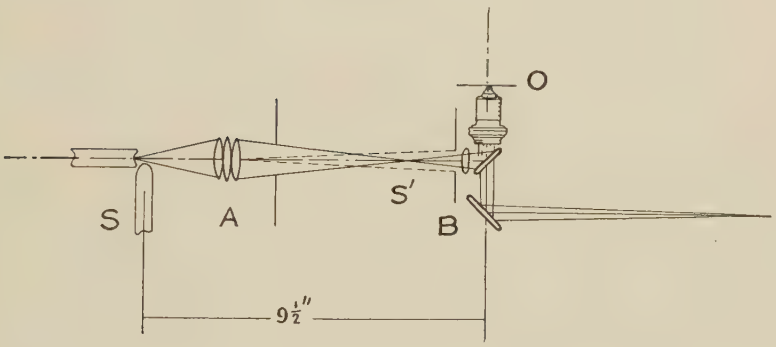


Fig. 460.

adjusted as shown in Figure 459. In this case it will be noticed that in the correct position the circle of light is located in the middle of the hemisphere and not centrally with the optical axis. The mirror illuminator is excellent for projecting with low powers. A little practice will enable one quickly to make these adjustments, and the results will amply repay for the time spent.

Some recent models are arranged, as shown in Figure 460, with the source of illumination 9½ inches from the axis of the microscope. Such an arrangement permits critical illumination and makes a more compact instrument with fewer adjustments. This reduction of the distance from the light source to the vertical axis is accomplished by a short-focus condenser and a supplementary lens to magnify and form a virtual image of the light source.

The light source S (Fig. 460), is imaged at S′ under a magnification of about 1.5 by the short-focus condenser A. B is an auxiliary condenser placed very close to the axis of the microscope and of such focal length as to form a real image of the condenser A in the back focal plane of the microscope objective. The auxiliary condenser B must also form a virtual image of the light source S′ in the conjugate focal plane of the objective. That is, the lens B places the light-source image to the left, at a distance from the objective equal to the distance to the right

from the image plane to the objective, or at a position such that the objective will image the light-source S on the specimen O. Thus, critical illumination results, and we have a short system of illumination performing the same as that represented in Figures 437 and 454.

The elimination of vibration is one of the difficult problems that most metallurgists have to overcome. No matter how rigid the apparatus, short sharp blows will produce vibrations which make it impossible to make good photomicrographs. There are a number of different devices in use ranging from simple to more elaborate appliances. Each user seems satisfied with his particular device. Probably the simplest and easiest to install consists of two planks, of a size suitable to hold the entire apparatus, and between them two inflated 3½-inch inner tubes or two circles of tennis balls.

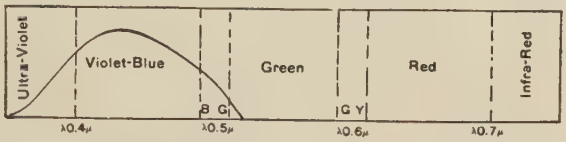
Another device much in use consists of a platform suspended from the ceiling, some consisting of simple chains or ropes, others of springs arranged with oil dampers below platform to check the spring movement. Another device, designed by Mr. Pafenbach of the Simonds Steel Co., Lockport, N. Y., consists of a submerged platform level with the floor, but suspended upon springs held by angle pieces projecting downward from crossbeams, also level with the floor. It seems that each one might best provide such means as are necessary in his particular location, but vibration, if it exists, should be eliminated. Vibration can be detected easily by observing the reflections from a small dish of mercury set upon the apparatus.

A focusing glass is a desirable addition, and almost necessary if one expects to obtain a sharp image upon the photographic plate, especially in high magnifications. As to the proper color of filter to use in metallography, there seems to be some differences of opinion, no doubt due to differences in plates, illuminants, objectives, and specimens used by different workers. Different colors have been experimented with, and it has been found that on iron and steel specimens a combination of green and yellow dominant wave length of 5500 Angström give the best results. Angström unit equals one ten-millionth of a millimeter. Often the appearance of the image upon the ground glass is made the basis of the proper filter to secure contrast desired, but suitable plates must be used to record such an image. Much difficulty is found in obtaining solid glass filters that will give the color desired, so it becomes necessary to use the glass-mounted, gelatine-stained variety. In the matter of plates one must select a plate suitable to the work and filter used.

Figure 461 shows the sensitive region of the ordinary plate, and if filters are used which transmit only green and yellow with very little blue, the exposure will be very long and the results not satisfactory. Figure 462 shows the sensitive region of the orthochromatic or isochromatic plates, and if filters are used, such as the B & G Wratten, transmitting wave lengths around 5500, this type of plate gives good results. The slower orthochromatic plates have a finer grain and are therefore best for photomicrographic work. Such plates as the Stanley Commercial or the Cramer Slow Iso will give good results. If heat-tinted specimens are used and there is much variation in colors, all of which one may wish to record, then the panchromatic plate should be used. Figure 463 shows that these plates are sensitive to a wide range of the spectrum.

The many factors involved, such as objectives, aperture, magnification, illuminant, filter, etc., make the keeping of records almost imperative. A method of standardizing a photomicrographic outfit has been described by Prof. Alexander Petrunkevitch

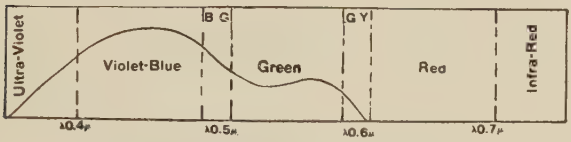
of Yale University in the Anatomical Record, Vol. 19, No. 5, October, 1920. While his article refers particularly to transparent photography, the same rules can be applied, namely, to determine the best location for each and every part of the apparatus, diaphragm apertures for different objectives, ray filters, plates, etc., and after establishing such record, one may make a picture of a given kind of object in the



Normal Spectrum Showing the Sensitiveness of Ordinary Photographic Plates.

(After Mees, and magnified as in fig. 139).

Fig. 461. — Sensitive region of the ordinary photographic plate.



Normal Spectrum Showing the Sensitiveness of Orthochromatic or Isochromatic Plates.

(After Mees; magnification as in fig. 139).

Fig. 462. — Sensitive region of orthochromatic or isochromatic plates.

Normal Spectrum Showing the Sensitiveness of Panchromatic Plates.

(After Mees; magnification as in fig. 139).

Fig. 463. — Sensitive region of panchromatic plate for a wide range of the spectrum.

minimum amount of time and be practically sure of the result without recourse to cut and try methods every time a picture is to be made.

The surface of the polished specimen must be flat. Any rocking on the grinding or polishing wheel will produce a cylindrical surface and the field in the microscope will have a band in focus while both sides may be out of focus. Also, the etching must be done properly to produce the contrast necessary to show the structure desired. Light etching has been found to give the best results with high powers. It is well again to emphasize the necessity of keeping all parts of the apparatus clean, not only all lenses, but all bearing surfaces. The apparatus should be protected with a rubber cloth covering when not in use. The instrument should be placed, if possible, where it is not exposed to the fumes of the chemical laboratory.

APPENDIX III

Committees' reports on the thermal analysis, preparation, etching, and photomicrography of iron and steel samples

TENTATIVE RECOMMENDED PRACTICE
FOR
THERMAL ANALYSIS OF STEEL[1]

ISSUED, 1925

I. Apparatus. — 1. The apparatus required for thermal analysis consists of a furnace for heating the specimen, a thermocouple, a potentiometer or galvanometer for measuring small changes in e. m. f., and a stopwatch or chronometer.

2. An electric-resistance furnace provided with a means of accurate and smooth temperature control should be used. A furnace of the Rosenhain type, or U. S. Bureau of Standards modification, is recommended. A good furnace is essential for accurate results. A neutral or reducing atmosphere or partial vacuum is desirable to protect the specimen from excessive oxidation.

3. The thermocouple may be of any approved type which has been calibrated either by the Bureau of Standards or against a secondary standard or by the melting point of pure metals (tin 231.9 deg. C., lead 327.5 deg. C., zinc 419.4 deg. C., aluminum 658.7 deg. C., silver 960.5 deg. C., copper 1083 deg. C.). A charge of at least 60 g. of metal should be used.[2] Base metal couples should not be used for temperatures exceeding 900 deg. C.

4. For recording data, a sensitive galvanometer or potentiometer and stopwatch or a recording galvanometer and a chronograph should be used.

II. Specimens. — 5. The size of specimen must be governed by the kind of furnace and the sensitivity of the instruments used. About ½ by ½ by 1 in. is satisfactory for most work.

The specimen should be normalized before making a thermal analysis.

NOTE. — This requirement applies to routine work only. For special researches exception may be made.

III. Procedure. — 6. The specimen should be heated and cooled at a uniform rate of from 5 to 10 deg. C. (9 to 18 deg. F.) per minute.

7. The specimen should be heated to a temperature of 100 deg. C. above the upper critical point and allowed to remain there fifteen minutes before cooling is begun.

8. Data may be plotted as desired. The inverse rate method is the simplest and most satisfactory for all general purposes and the most generally used.

In fixing the critical points, the temperature should be read at the cusp, or maximum point, of the inflection of the curve.

[1] Am. Soc. for Testing Materials, Vol. 25, 1925, pp. 890–891.

[2] The couple should be inserted in the specimen, insulated from it with mica or asbestos.

THE PREPARATION OF METALLOGRAPHIC SPECIMENS[1]

By H. M. Boylston, Cleveland, Ohio

I. Selection of Specimen. — Metallographic specimens should be so selected as to be representative of the metal from which they are taken. Where the piece has failed in service it is important that a specimen should be taken from near the failure and one considerably distant from it for comparison, or samples may sometimes be obtained from similar pieces which have stood up well in service.

When samples are taken from near a fracture, the metal very close to the fracture itself should be examined. The fracture edge should not be beveled and sometimes it is well to electroplate the fractured surface with copper (Rosenhain) in order to protect the fracture from beveling during subsequent grinding and polishing operations. Embedding the plated specimen in fusible metal as explained below is sometimes advisable.

Note should be made of the location of the specimen in the piece and the relation of the surface to be polished to the direction of forging and rolling. A sketch is very helpful in this connection.

II. Removal of Specimen. — Specimens are generally cut off with a hack saw. Tough steels like manganese steel and other austenitic material, hardened steels or even white cast iron which cannot be cut with a hack saw may be cut easily with a thin alundum or carborundum disk, $\frac{3}{32}$ inch thick and running in water if it is necessary to prevent tempering. If no cutting disk is available brittle specimens may be broken with a hammer although this means a rough surface to grind down later.

III. Dimensions of Specimen. — Much time is saved by keeping the specimen small within reasonable limits. A $\frac{1}{2}$ inch square or round piece is a good size unless the microscope is of such construction that a larger piece is necessary in order to prevent it from slipping through the stage. It is much easier and quicker to polish four pieces each $\frac{1}{2}$ inch square than it is to polish one piece one inch square. The thickness of the specimen should be less than the other dimensions if possible since the thicker the specimen the more difficult it is to hold it on the grinding and polishing wheels without rounding the surface. A $\frac{1}{2}$ inch square or round piece should be preferably not over $\frac{3}{8}$ inch thick. Very small specimens may be embedded in some fusible metal, sealing wax, fiber, or by mounting in suitable metal clamps. By these means the finest wire, turnings and even filings may be polished and examined. The following alloy, suggested by Campion and Ferguson, which melts in boiling water, is very useful in mounting small specimens:

Bismuth	50 parts by weight
Lead	30 " " "
Tin	25 " " "
Zinc	3 " " "

The inexpensive small iron cups known in the trade as "malleable gas caps," either $\frac{3}{8}$ or $\frac{1}{4}$ inch size, are very useful for holding the alloy and the specimen. The cap is heated to about 392 deg. F. (200 deg. C.) by placing it on an electric stove or on an iron plate heated by a Bunsen burner. The fusible alloy is then placed in it and melted. The temperature is then reduced until the cap and metal are just a little above 212 deg. F. (100 deg. C.) and the specimen to be polished is then pressed into

[1] Am. Soc. for Steel Treating Handbook.

the metal. The cap and its contents may then be solidified and cooled, and polished like any other specimen. If the nature of the specimen will allow it, it should be dipped into a saturated solution of zinc chloride before placing in the metal. The zinc chloride acts as a flux and cleans the surface of the specimen so that a better joint is made between it and the mounting metal. It is obvious that any metal that alloys with the mounting metal cannot be mounted in this way.

IV. Grinding and Polishing. — It was at one time thought necessary to grind and polish by hand but this is a tedious and slow method. Power grinding and polishing have now been in successful use for many years and are recommended except where very soft metals or alloys are to be prepared, when special precautions have to be observed. Grinding and polishing are generally carried out in three or more steps.

a. Grinding or filing to obtain a flat surface.
b. Rough polishing.
c. Fine polishing, generally including two or more steps.

(*a*) *Grinding.* — A medium fine and medium hard grinding wheel is generally used for this purpose. Grade 80-P alundum wheel or No. 2 French emery paper gives good results. Some grind on a coarse file but this is preferably restricted to soft metals. Grinding wheels may be mounted either vertically or horizontally and should be run at a speed of about 1200 R.P.M. The specimen should be kept cool on the grinding wheel by having water drip on it. Light pressure should be maintained on the specimen on all wheels or papers whether for grinding or polishing. The edges of the specimen should be beveled where possible in order to protect the cloth or paper from being cut. Specimens should be washed thoroughly in water after the grinding operation in order to remove any trace of abrasives. There are two reasons for grinding specimens: first, to remove the marks of the saw or cutting disk, and in order to know when this has been accomplished it is wise to hold the specimen so that the grinding marks are at right angles to those already found on the surface to be prepared. The second reason for grinding is to have an absolutely flat surface.

(*b*) *Rough Polishing.* — This may be done with grade FF Turkish flour emery powder or French emery paper No. 1. The powder should be suspended in water and used on a smooth wheel of some sort covered with 12-ounce canvas duck. Very little powder and much water should be used, and again the specimen should be turned 90 deg. so that the scratches produced by the powder or papers will be at right angles to those produced in grinding. The specimen should be washed thoroughly in water before passing to the next step, to remove all traces of abrasives. Some prefer to supplement the rough polish with French emery paper 0, 00, and 000.

(*c*) *Fine Polishing.* — Two or more steps are generally used. In the first step white reground tripoli powder or alundum powder 600 F may be used in water suspension and placed on a wheel covered with a fine grade of broadcloth. The cloth should not be too thick or a relief polish will be obtained. Plenty of water and not too much powder should be used.

The last operation may be performed with fine levigated alumina, grade No. 3, or with "superfine" magnesia powder. The best soft, high grade, jewelers' rouge powder may also be used. Levigated alumina or magnesia generally give better results than rouge, which is apt to scratch soft specimens. For this final operation "kitten's ear" silk broadcloth is preferable. When levigated alumina is used it should be suspended in water and squirted on the cloth disk by means of a devilbiss atomizer

or any other type having a broad orifice. If magnesia is used it will harden and cake slightly unless the cloth is removed each time and kept soaking in a weak solution (2 per cent) of hydrochloric acid (HCl) in distilled water. An exceptionally small amount of powder is necessary in the final polishing operation.

Except where otherwise indicated, all suspended powders may be placed on the cloth-covered disk by means of rubber-set varnish brushes. Some prefer to wash off the powder from the cloth in the final polishing and polish for a few moments on the cloth alone, which is thoroughly wet with water.

While the speed for grinding has been given as 1200 R.P.M. it is better to use lower speeds in the three other operations; namely, 300 to 600 R.P.M.

In every case specimens should be washed thoroughly after each stage of the operation.

Especially soft metals like lead alloys must be ground and polished by hand throughout the entire operation. In grinding the soft specimens the specimens should be rubbed over the file and not have the file passed over them.

V. Washing and Drying. — Specimens should be thoroughly washed in water after polishing and then washed in two baths of absolute alcohol and dried immediately by means of a blower. The best instrument for drying is some form of barber's hair dryer. Specimens should not be touched with the fingers after washing and drying or a greasy surface will be produced which will not etch evenly. Specimens should be carefully wrapped in cotton or placed in a desiccator until ready to etch and in the case of copper alloys etching and photography should be done as promptly as possible to avoid troubles due to tarnish.

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STANDARD METHODS OF METALLOGRAPHIC TESTING OF IRON AND STEEL[1]

Issued as Tentative, 1921; Adopted in Amended Form, 1924

MACROSCOPIC EXAMINATION

Preparation of Surface. — In order to show up both chemical and crystalline heterogeneity, sections of iron and steel are more or less deeply etched in order to bring out their macrostructure. In this way the persistence of the dendritic structure of castings even after much heat treatment and mechanical working, physical unsoundness such as blowholes, gas cavities, porosity, fine internal cracks and flakes, discontinuities of structure such as found in welding, flow of metal as in riveting, punching, hot pressing, and forging, etc., are brought out.

Suitable sections are cut, smoothed, and then ground on various grades of emery paper in order to obtain a smooth flat surface. In some cases it is necessary to continue polishing through No. 0 and No. 00 French emery papers. The sample

[1] Am. Soc. for Testing Materials. Standards, 1924, pp. 1154 to 1166.

ought to have a surface free from grease and dirt; if necessary it is then freed from all grease by cleaning with gasoline and then alcohol, when it is ready for immersion in the solution.[1]

Solutions Used in Etching. — Macroscopic etching of iron and steel was used as early as 1783 by Bergman. Many different solutions have been used and many of them are given by Campbell,[2] and more recently by Rawdon.[3]

Of the following solutions 1 (*a*) and 2 are recommended.

1. To show up segregation and the like:

(*a*) Hot concentrated hydrochloric acid used at about 100 deg. C. A deep etched specimen may be printed with printer's ink.

(*b*) Etching for 4 to 5 hours with 5 per cent picric acid in alcohol.

2. To show up variations in crystalline structure as well as segregation:

One to two grams of ammonium persulphate in 10 cc. of water. This is probably the best reagent for developing this phase of the structure in iron and steel.[4]

3. To show up the distribution of phosphorus:

Various reagents containing copper chloride are used. The copper coats those portions which are low in phosphorus and leaves the high phosphorus areas bright. It has recently been shown that nickel and other alloys give similar effects, also that oxide of iron acts in the same way. The accompanying list shows the various solutions which have been recommended:

Heyn. — Copper-ammonium chloride	10 g.	
Water	100 cc.	

A somewhat weaker solution is better, the specimen being etched two or three times in fresh solution if necessary. The liquid is gently agitated. The coating of spongy copper forming on the face of the specimen is easily removed with a swab of wet cotton. Portions high in carbon, sulphur, and phosphorus will have darkened. If the copper film adheres, a 0.5 per cent solution of ammonium persulphate will facilitate its removal.

Stead. — $CuCl_2$	10 g.	Dissolve salts in smallest possible amount of hot water and make up to 1000 cc. with absolute alcohol.
$MgCl_2$	40 g.	
HCl	10 cc.	
H_2O	20 cc.	
Alcohol to	1000 cc.	

For small specimens the reagent is applied drop by drop until structure is developed. The specimen is then washed with boiling water and then alcohol.

Another method is to wash off the deposited copper with ammonia and so increase the contrast.

Le Chatelier and Lemoine. — $CuCl_2$	10 g.
$MgCl_2$	40 g.
HCl	20 cc.
H_2O	180 cc.
Alcohol	1000 cc.

[1] For large sections various methods have been devised depending on the material. Surface grinding when carefully done gives excellent results.

[2] Proceedings, Am. Soc. Testing Mats., Vol. XV, Part II, p. 96 (1915).

[3] "Structure and Related Properties of Metals," Bureau of Standards Circular No. 113.

[4] Rawdon, "Macro-etching with Ammonium Persulphate," Scientific Paper No. 402, Bureau of Standards (1920).

Applied like Stead's reagent. Contrast can be increased by electrolysis, using a single battery cell, keeping the current below 50 milliamperes.

Rosenhain and Haughton. —

Fe_2Cl_6	30 g.
HCl	100 cc.
$CuCl_2$	10 g.
$SnCl_2$	0.5 g.
H_2O	1000 cc.

The copper adheres firmly. Pearlite areas remain bright. Ferrite darkened by deposited copper, the purest parts darkening the fastest. Pitting can be avoided by diluting the reagent.

Le Chatelier and Dupuy. —

Ethyl alcohol	100 cc.
H_2O	10 cc.
$CuCl_2$	1 g.
Picric acid	0.5 g.
HCl (concentrated)	1.3 to 2.5 cc., varying with material

Oberhoffer. —

Ethyl alcohol	500 cc.
H_2O	500 cc.
$SnCl_2$	0.5 g.
$CuCl_2$	1.0 g.
Fe_2Cl_6	30 g.
HCl	50 cc.

Humfrey. — Emery paper finish may be used for specimen.

Copper ammonium chloride	120 g.
HCl (concentrated)	50 cc.(±)
H_2O	1000 cc.

The addition of HCl causes the copper deposit to adhere. Etching is therefore started with the neutral solution and continued until all traces of the scratches have disappeared. Then in successive applications the acidity of this solution is gradually increased up to the maximum. Alloy steels etch better with solutions of weaker acidity. After wiping away the deposited copper and drying, the surface is lightly rubbed with fine emery paper and the relief portions brought out in strong contrast. The section may be printed with ordinary printer's ink applied to the surface by means of a roller.

Dickenson. — First etch with 10 per cent HNO_3. Then re-etch with:

Fe_2Cl_6	40 g.
$CuCl_2$	3 g.
HCl	40 cc.
H_2O	500 cc.

4. For etch tests to distinguish between wrought iron and steel, to develop the structure of welds, etc., the following rapidly acting reagents are recommended, the percentages given being by volume:

(*a*)	Hydrochloric acid (sp. gr. 1.19)	10 per cent
	Sulphuric acid (sp. gr. 1.84)	30 " "
	Water	60 " "
(*b*)	Nitric acid (sp. gr. 1.42)	25 " "
	Water	75 " "

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Oberhoffer, Stahl und Eisen, 1916, 36, Vol. I, p. 798.
Charpy and Bonnerot, Comptes Rendus, 1914, 165, p. 536.
Humfrey, Journal, Iron and Steel Inst., 1919, Vol. I, p. 273.
Dickenson, Idem, p. 294.
Howe, Metallography of Steel and Cast Iron, p. 601.

Methods for Indicating Distribution of Sulphur. — The distribution of sulphur is usually shown by the sulphur print method. A solution of 2 to 3 cc. of concentrated H_2SO_4 in 100 cc. of water is used to moisten a sheet of matt-finish photographic paper. The specimen with its surface smoothed either with a fine file or grinding wheel is pressed firmly on the paper on which a brown mark indicates the sulphur-rich areas. About 60 seconds is usually sufficient to give a good print. The paper is then washed and fixed in hyposulphite solution.

With larger sections the paper is placed on their polished surface with care so that no air pockets occur. If a very dilute solution is used and a longer "etch" several prints can be obtained. Fresh solution can be added with absorbent cotton should the paper tend to become dry.

References

R. Baumann, Metallurgie, 1906, p. 416.
Stead, "Sulphur and Iron," Staffordshire Iron and Steel Institute, March, 1908.
Hatfield, Cast Iron, p. 71, shows sulphur prints of pig iron.

Methods Used for the Location of Minute Cracks before Deep Etching. — Considerable differences of opinion have arisen as to the meaning of the results obtained by deep etching in transversely fissured rails, etc., because the presence of cracks in the material previous to etching had not been demonstrated. The following method, however, can be used to locate them. The sample after careful polishing is magnetized and then immersed in kerosene or a similar liquid containing very fine iron dust in suspension. The particles of iron dust collect upon the face of the specimen and orient themselves to correspond to the shape of the cracks because of discontinuity in the metal which causes a change in the density of the magnetic flux. The samples are then washed in clean kerosene to remove as much as possible of the excess iron dust which clings to the surface.[1]

According to several authorities their existence has been proven by annealing the specimens prior to etching, because a pronounced decarburized area then occurs around these cracks.

Method of Photographing. — The camera should be arranged so that the specimen is illuminated by vertical light. After certain kinds of etching, e.g., ammonium persulphate, the surface should be immersed in water, alcohol, or light oil. For large specimens the surface may be covered with oil or glycerine.

Printing the Surface. The surface obtained by deep etching may be printed with printer's ink applied with a roller. The printing can be done on a glossy paper in a

[1] Rawdon and Epstein, Technologic Paper No. 165, Bureau of Standards (1920).

letter press. For small samples of wrought iron deeply etched a reproduction can be made using an ordinary ink pad and applying the specimen as in block printing.

MICROSCOPIC EXAMINATION

Location of Test Pieces. — The location of the test piece for microscopic examination is of prime importance. In the case of a casting of steel or cast iron, the section ought to be cut perpendicular to the surface so as to show the variation of structure from the outside to the interior. In the case of forged and rolled metal both cross and longitudinal sections should be examined, their location being determined by the nature of the forging, etc. For crankshafts definite locations are given with reference to the tension test specimens. For guns, tangential specimens are required and for microstructure these should be cut parallel to the axis, etc. No one specimen is of necessity representative. The usual method of taking a cross-section from rods and bars while showing segregation of the constituents fails to reveal the usual lamination in such material for which a longitudinal section is necessary. The location of test specimens may be determined by a preliminary macroscopic examination.

In defective material, the sample should be cut adjacent to the fracture or defect. When necessary the fracture can be protected during grinding and polishing by coating it with a heavy deposit of electrolytic copper, molten lead-tin solder, or a mixture of litharge and glycerine. For hardened steel and other material liable to be tempered, fusible metals such as Rose's or Wood's alloys may be used.

Method of Polishing. — The method used for polishing specimens will depend primarily on the material to be examined and on the polishing equipment. In general, samples should not be over one inch square and their thickness should be less than the smallest dimension of the polished surface; otherwise there is a tendency to round off the edges during the process.

The softer material can be cut with a saw while harder metal may be cut with an emery disk or broken off with a hammer. A flat surface is at first obtained either by rubbing on a file held in a vise or by grinding on an emery wheel. In both cases it is necessary to avoid tearing the surface of the metal or causing it to flow. Perfectly smooth surfaces can be obtained by commercial surface-grinding machines.

Having obtained a flat surface in this way, the sample is next rubbed down on a series of emery papers, usually starting with No. 00 commercial followed by Nos. 0 and 00 French emery. These papers may conveniently be mounted on revolving disks. Rubbing on one paper is stopped as soon as the scratches from the last operation have been taken out. From the No. 00 French emery the specimen may be taken to a revolving disk covered with broadcloth, preferably running in a horizontal position at such a speed that the polishing powders are not unnecessarily thrown off. For ordinary work, two such disks will be sufficient, the first armed with well-washed carborundum, 65 or a similar grade, while the second may be armed with well-washed alumina. This is preferable to rouge because it is much cleaner.

To obtain a fine polish it is a mistake to try to save time by hurrying through the papers because if this is done, when the specimen is etched, innumerable fine lines will be revealed in the ferrite. In some cases the appearance of the ferrite is actually blurred because the metal distorted in the grinding and by the coarse grades of emery has not been subsequently removed. Under no conditions should buffing be tried, because this causes an actual flow of the metal and the structure is thereby obliterated.

No general rules can be laid down as to the method to be pursued, but common

sense will tell what is right and what is wrong. For example, in grinding on the emery wheel a copious flow of water must be maintained, otherwise the surface of the sample will heat up and the structure of the metal will be modified thereby.

For material of small size, such as sheet and wire, numerous methods of mounting have been devised. For wire, various mounting media such as wax, a mixture of litharge and glycerine, fusible metals and the like, can be used in a small brass container. For sheet metal, a pack can be built up of pieces of the sample with alternate layers of red fiber board, bakelite or other resistant material, the whole held together by two brass end pieces and two screws. The whole can then be polished down.

Methods of Etching. — The sample ought to be examined as polished in order to show up the non-metallic inclusions as well as cracks and other defects. In order to show up the structure of the metallic matrix various etching reagents have been used depending on the material being examined. The accompanying list gives the best of these reagents. For general work a 4 per cent solution of picric acid in ethyl alcohol is recommended. This darkens the pearlite in steel and leaves the ferrite or cementite bright as the case may be. Long etching with picric acid in alcohol will develop the grain structure in very low carbon steel and in wrought iron. This may be done more rapidly with a 2 to 4 per cent solution of nitric acid in ethyl alcohol (95 per cent). For showing up pearlite alone, picric acid in absolute alcohol is best.

To distinguish between ferrite and cementite in high-carbon steels, the usual method is to boil in the sodium picrate solution, which darkens the cementite.

For hardened and tempered steel, picric acid may be used, but after etching, washing under the tap, and flooding with alcohol, the specimen should be dried by an air blast, or if this is not available by shaking it in air. If the usual method of mopping on a soft towel be tried, the etching film will be spoiled.[1]

For the study of hardened and tempered steels under high magnifications other reagents have been devised such as those of Kourbatoff.

For distinguishing between cementite and phosphide of iron in cast iron, either heat tinting or boiling with sodium picrate may be used, as recommended by Matweiff. This attacks the iron phosphide but leaves the cementite unattacked.

For revealing the segregation of the phosphorus in steel, various reagents have been used, depending on the deposition of copper from a copper chloride solution, as given in the accompanying list of reagents.

Certain alloy steels, especially those high in the alloying elements, are very resistant to etching. For these special solutions have been devised such as ferric chloride for high-nickel material, caustic soda solution of hydrogen peroxide, etc., for high-speed steels.

In many cases after etching, the ferrite or cementite may be found to be more or less stained or colored. This can often be remedied by a light repolish on a chamois-skin pad. While this brightens up the ferrite or cementite, as the case may be, it markedly alters the appearance of the pearlite, giving it an abnormal structure, and therefore when this method is used, photographs should be so marked. The accompanying lists of reagents are commonly used.

[1] To dry specimens without the use of alcohol.:

After etching, wash in very hot water and dry in an air blast. With this method the results obtained are as good as with the older method of using alcohol after washing in water. After etching with dilute nitric acid solutions, steels in the unhardened condition do not show the stains which generally appear after drying with alcohol.

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Pamphlet No. 403, U. S. N. Bureau of Ordnance, October, 1916.

REAGENTS FOR ETCHING

(*a*) Solutions for Normal Iron and Steel

	(*a*)	(*b*)
Picric acid (Igevsky). —	4 g. picric acid. 95 cc. ethyl alcohol, absolute.	5 g. picric acid. 100 cc. ethyl alcohol (95 per cent).

Nitric acid. — 5 cc. HNO_3 (concentrated).
95 cc. ethyl alcohol (95 per cent).

Iodine. — 1.25 g. I.
1.25 g. KI.
1.25 cc. H_2O.
to 100 cc. alcohol.

Hydrochloric acid (*Martens and Heyn*, 1904) (*hardened steel especially*). —
1 cc. HCl (sp. gr. 1.19).
100 cc. alcohol.
May dilute to 500 cc. water: 1 of HCl, using very weak current.

(*b*) Solutions for Hardened Steel

Kourbatoff's Solutions. —

1. A. Solution. — 4 cc. HNO_3.
96 cc. amyl alcohol.
5 min., troosto-sorbite brown, austenite yellow, martensite white.

2. B. Solution — 1 part amyl alcohol
1 " ethyl " } (1).
1 " methyl "
1 " of 4 per cent HNO_3 in acetic anhydride (2).
Colors troostite and troosto-sorbite. Mix 1 and 2 just before using.

3. 2 parts methyl alcohol.
2 " ethyl "
2 " amyl "
1 " butyl "
3 " of 4 per cent HNO_3 in acetic anhydride.
For troostite.

4. 4 per cent HNO_3 in methyl alcohol to which 1/10 its volume of 4 per cent picric acid in ethyl alcohol is added.
Colors austenite, martensite, and troostite differently.

5. C. Solution. — 1 volume of 4 per cent HNO_3 in ethyl alcohol.
3 volumes saturated solution of nitrophenol in ethyl alcohol.
10 min. colors troosto-sorbite and martensite needles.

6. D. Solution. — 1 volume of saturated solution of ortho-nitrophenol in alcohol.
2 volumes of 20 per cent HCl in amyl alcohol.
Differentiates the various constituents.

7. 1 volume of HNO_3 in alcohol.
3 volumes of saturated solution of nitraniline.
Colors troostite, troosto-sorbite and martensite needles.

Benedicks. — 5 per cent meta-nitrobenzol sulphonic acid in alcohol 0.15″ darkens martensite more than austenite.

(*c*) Solutions for Carbides, Etc.

Kourbatoff. — 2 g. picric acid.
98 cc. of 25 per cent NaOH in water.
Used boiling 5 to 10 min. Cementite colored. Also Fe_nW, Fe_2W_2C, etc., in tungsten steels while WC is unattacked. Ferrite unattacked.

Matweieff. — Neutral sodium picrate washed several times with distilled water.
Solution used boiling. 20 min. Iron phosphide attacked, cementite unattacked.

Yatsevitch. — 10 cc. H_2O_2 (commercial).
20 cc. of 10 per cent NaOH in water.
10–12 min. For high-speed steel. Use fresh. Tungsten carbide darkened.

Hilpert and Colver-Glauert. — 3 to 4 per cent of a saturate solution (aqueous) of SO_2 in alcohol or water.
7 sec. to 1 min. For non-pearlitic steels and pig iron.

Murakami. — 10 g. potassium ferricyanide.
10 g. potassium hydroxide.
100 cc. water.
Use hot. Distinguishes between carbide and tungstide in high-speed and in tungsten steels.

(*d*) Solutions for Alloy Steels

Ferric chloride. — Fe_2Cl_6 5 g.
HCl 50 cc.
Water 100 cc.
Used for austenitic nickel steels.

Electrolytic. — Aqueous solution of 0.5 per cent NaOH with very weak current. On 110 volt circuit use two 4 c. p. lamps in series, connected with two wire terminal (platinum wire preferable). Flood specimen's surface with solution. Make contact with one wire at side and dip the other with the solution, moving it around to obtain uniform etch. Used for stellite, high chrome, etc.

METHODS FOR IDENTIFICATION OF NON-METALLIC INCLUSIONS

Stead. — Dilute H_2SO_4 (1 : 3 H_2O). Bubbles from sulphides, none from silicates.

Law. — Uses an acid solution of lead or cadmium salt in gelatine. The sulphides form deep brown or yellow stain of cadmium or lead sulphide.

Electrical etching solution: Distilled water with 0.002 per cent ammonium chloride or caustic potash solution used boiling. After a few minutes wash and dry with alcohol.
MnS unaltered.
Oxide completely removed.

Matweieff. — Action of hydrogen at high temperatures.
Oxides (MnO FeO) — reduced.
Silicates — unaffected.
Sulphides — unaffected.

Action of vapor of water at high temperatures.
Oxides — attacked.
Silicates — unattacked.
Sulphides — unattacked.

Action of organic acids.
Oxides — unattacked.
Silicates — unattacked.
Sulphides — attacked.
Distinction between FeO and MnO.
Reduction by hydrogen — repolished.
Dilute alcohol solution of $FeCl_3$.
If colored deep — MnO with some FeO.
MnO alone is not reduced.
If colored feebly — FeO.
Distinction between FeS and MnS.
FeS — colored by solution of tartaric acid.
MnS — very feebly colored.

Rohl. — Sulphides 1 per cent acetic, citric, oxalic, or picric acid in water.
FeS always more readily blackened in one minute. MnS blackened slightly after 45 seconds.
Picric acid gives most uniform results.
1 per cent acetic or picric acid in ethyl alcohol can be used.
Etching by picric acid (4 g. acid + 100 cc. amyl alcohol then by dilute HNO_3) (4 cc. + 100 cc. amyl alcohol) then by concentrated hot NaOH solution. Dark brown color due to sulphides.
Sodium acetate 2 per cent aqueous — 1 minute.
FeS — brownish tint.
MnS — very light.
Reduction Tests.
(1) $HgCl_2$ solution.
Sulphides covered with Hg especially FeS.
Repolishing (softly) FeS — corroded, MnS — not corroded.
(2) $AgNO_3$ solution. (3 per cent solution boiling.)
FeS — uniform violet blue.
MnS — dove gray slightly darkened.
Repolishing:
FeS — reddish violet
MnS — blue gray.
Rohl's Method of distinction:
(1) Organic acid 1 per cent in ethyl alcohol with 5 minutes etching.
FeS darkens more than MnS.
(2) A short preliminary etching. With 1 per cent picric acid in ethyl alcohol followed by tempering to dark yellow.
FeS — a beautiful dark blue to reddish violet.
MnS — dull gray to bright white.

Sulphides

McCance. —

Whiteley's Reagent: 5 g. gelatine + 20 cc. H_2O, soak for one hour and add 15 cc. glycerine. Heat till clear, add 0.05 g. tartar emetic in 1 cc. H_2O, filter and add 1 cc. dilute H_2SO_4. Apply warm.
Yellow ring forms around sulphides.

McCance's Reagent. Replace tartar emetic by 0.1 g. $AgNO_3$.
Black stain indicates sulphide.

For Silicates and Oxides

McCance. —

A.	HF	2 cc.	For steels, about 3 sec. darkens sulphides, and silicates. Oxides unattacked.
	absolute alcohol	98 cc.	
B.	HF	8 cc.	
	H_2O	42 cc.	
	Alcohol	50 cc.	

Comstock. — Uses boiling alkaline picrate of soda. MnS blackened and roughened. Silicates and oxides unaffected.

References

Stead, Iron and Steel Magazine, IX, p. 105.
Law, Journal, Iron and Steel Inst., II, 94 (1907).
Matweieff, Revue de Métallurgie, VII, p. 447.
Rohl, Journal, Iron and Steel Inst. Carnegie, Memoir, IV, p. 28 (1912).
McCance, Journal, Iron and Steel Inst., 1–239 (1918).
Comstock, Translations, A. I. M. E., LVI, 553 (1916).

Bibliography of Etching

Fry, "Etching to Develop Overstrain," Stahl und Eisen, Vol. 41, pp. 1093–1097 (1921); Chemical and Metallurgical Engineering, Vol. 27, p. 349 (1922). Method brings out markings in overstrained steel. After polishing, the specimens are heated to 200 deg. C. for one-half hour.

Etching Solution:

Hydrochloric acid (concentrated)	40 cc.
Water	30 cc.
Ethyl alcohol	25 cc.
Cupric chloride crystals	5 g.

After immersion, the specimen is rubbed with finely powdered cupric chloride on a rag moistened with the etching solution until desired contrast is obtained, dried without rinsing, washed with alcohol and again dried. The dark portions are due to the presence of iron hydride and indicate the amount of plastic deformation the metal has received.

Gill and Bowman, "Metallography of High-Speed Steel," Transactions, Am. Soc. Steel Treating, Vol. II, pp. 184 to 205. Picric acid used for annealed samples, 6 to 8 per cent HNO_3 in alcohol best for hardened specimens. A solution of NaOH and H_2O_2 and a solution of $K_3Fe\,(CN)_6$ used for tungstides.

Krivobok and Sauveur, "Use of Sodium Picrate in Revealing Dendritic Segregation in Iron Alloys," Am. Inst. Mining and Metallurgical Engrs., February, 1924.

Loskicwiz, "Time of Attack of Micrographic Reagent on Iron-Carbon Alloys," Revue de Métallurgie Mémoires, Vol. XIX, pp. 681 to 687 (1922). Gives time of etching with picric and nitric acid solutions in alcohol at three temperatures (16, 24, and 35 deg. C.) for plain carbon steels. Gives also curves showing time of attack for pearlite, sorbite, troostite, and martensite in a 0.9 per cent carbon steel, and a table of basic reagents used to color cementite.

Pilling, "Micrographic Detection of Carbides in Ferrous Alloys," Am. Inst. Mining and Metallurgical Engrs., February, 1924.

Silicon steels up to 6 per cent are attacked by water during polishing. It is necessary to use alcohol as polishing lubricant in the last stages of preparation and to avoid all etching reagents having an aqueous base. Boiling alkaline sodium picrate solution attacks the silico-ferrite.

A new reagent consists of a dilute solution of nitric acid and methyl alcohol in nitro-benzol. Make an anhydrous stock solution of 20 per cent nitric acid in methyl alcohol. The etching reagent consists of 40 drops of this solution in 50 cc. of nitro-benzol. Etch by immersion for 20 seconds. Store in dark-colored bottles.

Strauss, B., and Fry, A., "Formation of Cracks in Boiler Plates," Stahl und Eisen, Vol. 41, p. 1133. Metallographic illustrations obtained by same reagents as given under Fry, above.

MEANS FOR THE IDENTIFICATION OF NON-METALLIC INCLUSIONS

As Polished

FeS.	Brownish yellow.
MnS.	Slate blue, smooth.
FeS_xMnS_y.	Slate blue to brown, may show duplex structure.
FeO.	Slate blue, rough, a little darker than MnS.
MnO.	Similar.
Mn — Silicate.	Greenish tinge, smooth and greasy.
Fe — Silicate.	Black and greasy.
Al_2O_3.	Tiny hard rounded grains, never elongated by rolling, etc.
Sand Grains.	Angular form, convex side, greasy appearance standing in high relief.
Titanium nitride or cyanonitride.	Pink or yellow cubic crystals.

	Sulphides	Oxides	Silicates
H_2SO_4 (1 : 3 H_2O).	Gas bubbles	No action.	No action.
Pb or Cd salt in gelatine.	Brown or yellow stain.	" "	" "
McCance's Reagent, $AgNO_3$ in gelatine.	Black stain.	" "	" "
Acetic, citric, oxalic, etc.	Attacked.	" "	" "
Boiling sodium picrate.	Black and rough.	" "	" "
H or H_2O at 600 deg. C.	No change.	Reduced or attacked.	" "
2 cc. HF in alcohol, 3 sec. etch.	Darkened.	No action.	Darkened.
Electrolysis (0.002 per cent. NaOH).	No change.	Removed.	No change.

	FeS	MnS
As polished	Brown-yellow.	Slate blue — smooth.
Tartaric acid	Colored	Colored, less.
1 per cent picric alcohol. 5 min.	Blackened.	Less so.
Ditto. Heat tint to dark yellow	Blue-violet.	Dull gray white.

	FeO	FeO_xMnO_y	MnO
H at 600 deg.	Reduced.	Reduced.	Unreduced.
Electrolysis (0.002 per cent NaOH)	"	"	"
Alcohol Fe_2Cl_6 solution after electrolyzing and repolishing	Feeble color.	Deep color.	Not reduced.

PHOTOMICROGRAPHY [1]

By Walter M. Mitchell and H. M. Boylston

The photomicrography of polished and etched specimens of metals with the aid of a microscope is important as a means of securing records of their microstructure for reference and future examination. The production of such photographs, called photomicrographs (not microphotographs, which are merely photographs of microscopic size), requires proper care and skill in the manipulations, if satisfactory results are to be obtained. Before photomicrographic work is attempted, four things are essential:

(*a*) The microscope and the source of illumination must be in proper adjustment, individually and with each other.

[1] Am. Soc. for Steel Treating Handbook.

(*b*) The microscope must be so mounted that it will be free from vibration. Ordinary vibrations are harmless if all parts of the apparatus are tightly clamped together.

Vibrations from steam hammers and from railroad trains passing close to the laboratory can be minimized by placing several inches of sponge rubber under the legs of the stand. If this does not correct the trouble the outfit may be suspended from the ceiling with spiral springs, or a spring suspension stand may be used.

(*c*) Specimens must be polished flat and free from scratches.

(*d*) If the specimen is etched, the structure should be as clean cut as possible. Lighter etching than that used in low power work is necessary for good results at high magnifications.

Magnifications. — It is recommended that the following standard magnifications be used in making photomicrographs (expressed in diameters): for ferrous materials, 10, 50, 100, 250, 500, 1000, 2000, 5000; for non-ferrous materials, 10, 25, 50, 75, 100, 150, 200, 250.

The term photomacrograph is generally applied when the magnification is less than 10 diameters. In photomacrography the following magnifications are commonly used (expressed in diameters): ½, 1, 1½, 2, 2½, 3, 5.

Generally speaking, it is better to use a higher power objective rather than a lower for obtaining a given magnification if maximum resolution is desired, but too short a bellows length (projection distance) is also to be avoided.

Lenses. — In the following table are given the various lenses and lens combinations which are convenient for obtaining different magnifications.

Lenses for Various Magnifications

Linear Magnification in Diameters	Objective		Ocular
	Type	Focal Length (approximately) mm.	Type[1]
½ to 2	Photographic Tessar IIb	153	None
2 to 10	Photographic Micro-Tessar or Micro-Planar	72	None
10 to 20	Photographic Micro-Tessar or Micro-Planar	48	None
20 to 30	Photographic Micro-Tessar or Micro-Planar	32	None
30 to 75	Achromatic	32	Huyghens or similar
75 to 150	Achromatic	16	Huyghens or similar
200	Achromatic or Apochromatic	8	Compensating or projection eyepieces for use with apochromats
200 to 500	Achromatic or Apochromatic	8 4	....
1000 to 5000	Oil Immersion	2	.....

[1] The magnifying power of the ocular should be such that the desired size of projected image can be obtained with a moderate length of bellows.

Determination of Magnification. — Where extreme accuracy is desired, magnifications should be measured experimentally with the aid of a stage micrometer. This is preferably made of metal and placed on the microscope stage in place of the specimen. The image of the rulings on the micrometer is then projected on the focusing screen and the magnification determined directly by means of a small scale, either ruled on the focusing screen or placed over it. Stage micrometers ruled to 0.1 and 0.01 mm. are the most convenient. The projection distance is the distance in millimeters or inches from outside focus of eyepiece lens to nearest (ground) surface of focusing screen. Charts may readily be prepared for any combination of eyepiece and objective with the projection distance as one coördinate and magnification as the other.

For approximate determination of magnifications which are sufficient for routine work the following formula may be used:

$$M = \frac{DM'}{250}$$

where M is the magnification to be determined, D the projection distance measured in millimeters, and M′ the magnification of a particular combination of eyepiece and objective at 250 mm. (10 inches) projection distance. The values of M′ are generally supplied by the manufacturer in a table accompanying the microscope, and may be given as the magnification at the eye, since the lens of the eye produces on the retina an image with a magnification corresponding to that obtained in projection at a distance of 250 mm. from the outer focus of the eyepiece. Since this outer focus of the eyepiece is very close (about 3 mm. away) to the lens of the eyepiece the projection distance may be measured roughly by determining the distance from the eyepiece lens to the near side of the focusing screen.

Illumination of Specimens. — For use with objectives of 32 mm. focal length or less, all of which are used in combination with oculars, vertical illumination (i.e. normal to the surface under observation) is usually necessary. Either the plane-glass or mirror type of illuminator (the latter including the totally reflecting prism) in which the reflector is placed between the objective and the ocular may be used. For the best results, the condition of "critical illumination" should be obtained; that is, the optical distance from the source of light (real or apparent) to the surface of the specimen should equal the distance from the specimen to the focal plane of the ocular, or, in other words, the source of light should be approximately imaged on the specimen. The mirror or prism type of illuminator is not suitable for very short focus objectives (4 mm. or less), since it obscures a relatively large portion of the lens aperture.

With objectives of the photographic type, vertical illumination is obtained by inserting the illuminator (plane glass) between the lens and the surface of the specimen. Oblique illumination may be obtained by directing a beam of light so that it strikes the surface of the specimen obliquely or, in a lesser degree, by rotating the reflector of the vertical illuminator. A special form of oblique illumination known as "conical illumination" and methods for obtaining it are described by H. S. George in the Transactions, A. S. S. T., Vol. IV, 1923, page 140.

For lenses of the photographic type of more than 48 mm. focal length the illumination should be diffused, for example daylight; or oblique, as obtained by directing a beam of light upon the specimen obliquely from one side; or vertical, by means of a large plane glass placed between the lens and the object. In order to increase the

size of the field, which otherwise would be restricted in diameter to that of the photographic lens, a relatively large planoconvex lens should be placed between the reflecting plane glass and the source of light, the lens being located so that the optical distance between it and the photographic lens equals the focal length of the planoconvex lens. Moistening the surface of the specimen with water, glycerine, or oil, or even immersing the entire specimen in alcohol or water, will often be found desirable for the purpose of increasing the contrast in the photograph.

In the case of fractured specimens, a good reproduction of the fractured surface may be readily obtained by using two sources of artificial light of unequal intensities. Place one source of light on each side of the specimen. A reflector may be used in place of the weaker light source if desired. The second, or weaker, illuminant serves to neutralize partially the deep shadows cast by the stronger one and so produces a good relief effect.

Photographic Plates. — The most convenient size of plate or film for the average laboratory is 4 x 5 inch, but economy may be effected where a great many negatives are made daily by using a size 3¼ x 4¼ inch. Occasionally a 5 x 7 inch negative or even an 8 x 10 inch negative will be advantageous, especially in macrographic work.

Various types of plates are listed below because of the difficulty in some localities of obtaining some preferable types. It is simpler and easier, however, to learn how to use one plate or film to the best advantage and stick to it. The Wratten M (panchromatic) plates have a special fine-grained emulsion which gives a very desirable combination of detail and contrast. This detail and contrast may be varied according to requirements by the use of monochromatic color screens. The Wratten filters, or screens, are as follows: B (green), F (red), K (yellow), etc. Nothing is gained by using these plates unless a monochromatic screen is used in conjunction with them.

While it is necessary, for the best results, to handle and develop Wratten M plates in complete darkness, the makers include in each box of plates a card giving the proper time of development for that particular emulsion. Allowance is made for low contrast, normal contrast, great contrast and varying temperatures of developer; thus an opportunity is afforded for the exercise of judgment on the part of the operator depending upon the conditions surrounding the making of the negatives. There are other panchromatic plates but they do not give such good results.

One of the disadvantages of panchromatic plates is their poor keeping qualities, especially in warm weather.

The following brands of orthochromatic (isochromatic, i.e. sensitive to yellow light) plates may be used in conjunction with yellow or green screens with complete satisfaction, but they cannot be used with a red filter:

Medium Speed. — Standard Orthonon; Cramer Medium Iso; Stanley; Hammer Special Nonhalation Ortho.

Slow Speed. — Cramer Slow Iso; Hammer Slow Ortho.

These plates are of average contrast, fine grained, and may be used for structures which show considerable contrast.

Plates giving greater contrast but requiring slightly longer exposure are:

Medium and Slow Speed. — Cramer Commercial Isonon; Stanley Commercial; Hammer Commercial Ortho.

Photographic Films. — The use of films for photomicrographic work has much to commend it. The cut films are easily handled in frames which hold them flat in the ordinary plate holder. Other frames of special non-corrodible material are available

for holding the films in the developer tank and fixing box. Films do not crack or break during storage or shipment and take up less space. They apparently stay flat during exposure since the negatives do not show "out of focus" areas. They are not yet available in the Wratten M emulsion but can be had in the Standard Orthonon type, and should be used in conjunction with a Wratten B or a K filter for the best results.

Monochromatic Filters. — Since all photographic plates are most sensitive to blue light, for which the objective lenses are not corrected, and since the yellowish green rays are those most easily distinguished at the focusing screen, it is necessary to absorb the blue rays with a suitable color screen or filter. Through their use a good achromatic lens gives just as good or better results as an expensive apochromat. Moreover, apochromatic lenses always have a residual spherical aberration resulting in lack of flatness of field in spite of so-called compensating eyepieces. Most American achromats are corrected for the very color obtainable with a Wratten B (green) filter, so the latter is obviously the correct one to use in conjunction with a plate which is sensitive to green light, such as the Wratten M or the Standard Orthonon, Cramer Iso or Hammer Special Nonhalation Ortho. Some prefer a Wratten K_1, K_2, or K_3 filter, while others prefer the Wratten M plates and the Wratten B (green) screen. If the exposure is correct (and there is considerable latitude allowed) and the development correct, any gradation of detail and contrast may be obtained with this combination at low, medium, or high magnification. The green color is also the most restful to the eye in visual work, especially if a white ground screen is used in combination with it.

Red screens (Wratten F) give more contrast and somewhat less detail than green (Wratten B) and are preferable in macrography where minute detail is less important than maximum contrast.

Theoretically, it would seem as if a blue filter (short wave length) in conjunction with a proper plate would give better results where fine details are to be photographed at high magnification, but this does not appear to be borne out in the experiences of many of the most careful workers. Light of short wave length may have its advantages in the case of stained transparent objects using transmitted light, but it appears to offer no special advantage in metallography.

For the best results the filter used should be kept in place while adjusting the final focus at the focusing screen.

Some workers use a liquid filter such as a nickel chloride solution for green, or one of the green Aniline dyes, and for a yellow filter a saturated solution of potassium bichromate, but it is difficult to keep the solutions free from air bubbles and at the proper strength because of evaporation. A well made glass filter will last indefinitely if maintained at a point in the beam of light where the heat from the light is at a minimum.

Exposure of Negative. — The time of exposure varies with the following factors:

(*a*) *Character of Specimen.* — Bright or light-colored structures, such as free ferrite or free cementite, require shorter exposures than dark ones like troostite, sorbite, pearlite, etc., and generally speaking, the darker the general appearance of the structure and the less contrast it contains the longer will be the proper time of exposure.

(*b*) *Speed of Plate.* — The faster the plate, the shorter will be the exposure required.

(*c*) *Intensity of Light.* — With a good carbon arc light and with iris diaphragms

and settings of the optical system arranged to give critical illumination, the exposure required at 100 diameters magnification using direct current, a Wratten M plate and a Wratten B filter, is approximately eight seconds. With alternating current under the same conditions the required exposure is twelve seconds. With a tungsten arc light which can be used only with direct current, and other conditions as stated, the required exposure is about forty-five seconds. With a 6 volt, 24 watt, automobile headlight type of Mazda incandescent lamp the corresponding exposure would be sbout sixty seconds.

(*d*) *Color of Light.* — If the proper exposure with carbon arc and green (Wratten B) filter at 100 diameters is eight seconds, the exposure under similar conditions with a red (Wratten F) filter would be approximately six seconds for a Wratten M plate. For a yellow filter (K_2) and other conditions the same as stated the exposure would be approximately four seconds.

(*e*) *Magnification Used.* — If the exposure required at 100 diameters is eight seconds the exposure required at 400 diameters would be approximately forty seconds or at 1000 diameters it would be approximately sixty seconds.

(*f*) *Size of Opening in Iris Diaphragms.* — The size of the opening in the iris diaphragm between the source of light and the first condenser in most American instruments controls, to a considerable degree, the resolution of detail in the image; the smaller the opening the greater the resolution, but it is also true that the smaller the opening the longer the exposure.

If the correct exposure time has not been obtained from the information given above then this should be determined by experience and trial. Adopt a system of making all exposures at standard magnifications of, say, 50 X, 100 X, 500 X, 1000 X, 2000 X, 5000 X. If this is done, after a little experience, the proper exposure time can be estimated by the appearance of the image on the focusing screen. The correct exposure time may be easily determined by exposing successive portions of a test plate to progressively longer exposures. Draw slide out of the plateholder so as to expose one inch of the plate, expose for five seconds, draw the slide out another inch, expose again for five seconds, and repeat until the whole plate is exposed. On developing, that strip which is correctly developed will indicate the proper exposure time. In any case the exposure should be sufficiently long so that the darker portions of the structure will be fully exposed; otherwise no details in these will be recorded and they will appear dead black in the final print.

Plate Developers. — The safest and most convenient developer is generally that recommended by the plate or film manufacturer who is in a position to know what developer is best suited to the particular emulsion furnished. Directions are generally given on a card or pamphlet found inside the box of plates or films.

The developer recommended by the manufacturer of Wratten M plates is as follows:

PYRO SODA DEVELOPER

Developing Formula for Wratten and Wainwright M Plates

(Do not wet the film before applying developer.)

		Avoirdupois	Metric
A.	Potassium metabisulphite	250 grains	17 grams
	Sodium sulphite (desiccated)	2½ ozs.	70 grams
	Pyrogallic acid	¾ oz.	20 grams
	Water to	32 ozs.	1000 cc.

Dissolve in order given.

		Avoirdupois	Metric
B.	Sodium carbonate (desiccated)	2⅔ ozs.	75 grams
	Potassium bromide	15 grains	1 gram
	Water to	32 ozs.	1000 cc.
	Use equal parts of "A" and "B"		

Typical Time of Development with above Formula in Minutes.
(Time varies somewhat with different batches of plates.)

Temperature	Diminished Contrast	Normal Contrast	Great Contrast
50 degrees F.	2.0	3.2	6.4
65 degrees F.	1.0	1.6	3.2
80 degrees F.	.5	.8	1.6

Pyro developers are readily adapted to tank or time development and it is nearly impossible to overdevelop with them.

For other plates and films the choice of a developer is largely a matter of personal preference.

The two developer formulæ which follow, the result of many trials and experiments, are a normal developer for general work and a contrast developer, which will give maximum contrast, for contrast and lantern plates. They are recommended as having good keeping qualities, working rapidly, free from stain, and inexpensive to prepare.

Make up a stock solution as follows:

Normal Plate Developer

		Avoirdupois	Metric
A.	Water (distilled)	32 ozs.	1000 cc.
	Sodium sulphite (desiccated)	1 oz.	30 grams
	Metol or Elon	60 grains	4 grams
	Hydrochinone	60 grains	4 grams
	Potassium bromide	30 grains	2 grams
B.	Water (distilled)	32 ozs.	1000 cc.
	Sodium carbonate (desiccated)	¾ oz.	22 grams

Dissolve Elon before adding sodium sulphite; otherwise it may be reprecipitated: add other ingredients in order given.

For a working strength developer, use equal parts of A, of B, and of water.

Contrast Plate Developer

		Avoirdupois	Metric
A.	Water (distilled)	32 ozs.	1000 cc.
	Sodium sulphite (desiccated)	2¾ ozs.	80 grams
	Hydrochinone	½ oz.	15 grams
	Potassium bromide	¼ oz.	8 grams
B.	Water (distilled)	32 ozs.	1000 cc.
	Caustic potash	1⅔ ozs.	48 grams

For a working strength developer, use equal parts of A, of B, and of water. Ordinary tap water may be used if free from iron salts.

The stock solution will keep indefinitely if stored in well filled, tightly corked bottles.

Either of the above developers in mixed solution may be used until exhausted, five ounces of the mixed solution being sufficient for one half dozen 4 x 5 inch plates

or their equivalent. Developer should be used at a temperature of 65 deg. F. This is very important, since higher temperatures will give failure due to "frilling" of the emulsion. At 65 deg. F. development of a properly exposed plate will be complete in three to five minutes; longer time will increase the density of the negative, necessitating longer printing time, and increase the contrast. Insufficient development under above conditions indicates under exposure.

After the plates are developed they should be rinsed thoroughly in water and fixed in the following fixing bath:

CHROME ALUM FIXING BATH

	Avoirdupois	Metric
Water	32 ozs.	1000 cc.
Hypo	12 ozs.	350 grams

When dissolved, add 1⅔ ozs. (50 cc.) of the following hardener solution:

	Avoirdupois	Metric
Water	3½ ozs.	100 cc.
Chrome alum	185 grains	12 grams
Sodium bisulphite	308 grains	20 grams

This bath ceases to harden the gelatine film after keeping for several days, so that in warm weather if the film tends to soften a fresh fixing bath should be prepared daily.

In cold weather use one-half the quantity of hardener solution. If precipitation of dirty white and finely divided sulphur occurs, as sometimes happens while mixing or on long standing, it is better to throw the bath away and prepare a new one. Do not use old or discolored fixing baths.

The following fixing bath, although it will not harden the gelatine film so much as the chrome alum bath, maintains its hardening properties on keeping and is, therefore, preferable for use in hot weather.

FIXING BATH FOR HOT WEATHER

	Avoirdupois	Metric
Water	64 ozs.	2000 cc.
Hypo	16 ozs.	500 grams

When dissolved, add the following hardening solution:

	Avoirdupois	Metric
Water	5 ozs.	150 cc.
Alum (powdered)	1 oz.	28 grams
Sodium sulphite (desiccated)	1 oz.	28 grams
Glacial acetic acid	1 oz.	30 cc.

When using the above solution, fixing will take about double the time (20 minutes as a minimum) required to dissolve the unreduced silver emulsion, which is determined by noting when the grayish white color disappears from the back of the negative. After thoroughly fixing, negatives should be washed for one-half hour in running water to remove all traces of hypo, then stood on a drying rack so that they will drain from one corner. Films should be suspended from one corner to dry.

A convenient test for determining whether washing is complete, which may also be used for prints, is made as follows:

Test for Completion of Washing

	Avoirdupois	Metric
Water	8 ozs.	240 cc.
Potassium permanganate	8 grains	½ gram
Sodium carbonate	10 grains	⅔ gram

Allow the excess water to drain from the partially washed negative or print into a graduate and add a few drops of the above solution. If the color remains pink, washing has been complete; but if it turns yellowish, hypo is still present. This is a very sensitive test and is useful where speed is necessary.

Over- and Under-Exposed Negatives. — Underexposed negatives will lack detail in parts corresponding to the darker regions of the specimen, while overexposed will be "flat"; i.e. full of detail without much contrast. Whenever possible, it is better to repeat the exposure, making another negative giving double, or half the exposure time, as the case may be, than to attempt to "doctor" a poor negative. Nothing can be done with underexposure, as detail lacking in the negative originally cannot be introduced by any chemical process. Contrast may be increased in overexposed negatives, but the process is uncertain and the intensified negative is rarely permanent. Repeat the exposure, or use a contrasty paper when making prints.

Overdeveloped negatives are very dense, requiring a long time in printing. These may be reduced in the following solution:

Reducing Solution

		Avoirdupois	Metric
A.	Water	1 oz.	30 cc.
	Potassium ferricyanide	15 grains	1 gram
B.	Water	32 ozs.	1000 cc.
	Hypo	1 oz.	28 grams

Mix A and B and immerse the plate in the solution until sufficiently reduced. Wash thoroughly and dry in the usual manner. The above solutions (A and B) keep well, but the reducer obtained by mixing A and B will remain active for only a short time.

Printing. — Prints are made from the negative in the usual way. Use a constant light source and always place the printing frame at a constant distance from it (18 inches for a 100 watt bulb). The proper exposure for the print may easily be estimated from the density of the negative after a few trials. If many prints are to be made a special printing machine is a good investment.

Satisfactory papers are Azo, Cyco, and Velox. Azo is somewhat slow to print but is cheap in price and easy to work with, and an excellent paper for general use. It is made in four grades, Nos. 1 to 4. The latter gives most contrast and is recommended for the average negative. Cyco prints more rapidly than Azo and is made in three grades: Contrast, Normal, and Soft. The former is very contrasty, and the latter very soft and intended for very contrasty negatives. Normal Cyco is for general use and is about equivalent to No. 3 Azo. Velox is made in four grades in the same order as Azo. It is more expensive than Azo and has no advantage over it. It is to be remembered that "hard" or "contrasty" papers are to be used for "soft" or "flat" negatives, and vice versa. Always use paper with glossy surface.

There is no single developer that will give the best results with all makes of papers. It is safe to use that recommended by the maker of the paper. For the above mentioned papers, the following may be relied upon to give good results.

Make up a stock solution as follows (dissolve in the order given):

	Avoirdupois	Metric
Warm water (distilled)	16 ozs.	500 cc.
Sodium sulphite (desiccated)	1¼ ozs.	35 grams
Metal or Elon	30 grains	2 grams

When completely dissolved, add:

	Avoirdupois	Metric
Hydrochinone	120 grains	8 grams
Sodium carbonate (desiccated)	1¾ ozs.	50 grams
Potassium bromide	15 grains	1 gram
Sodium citrate	15 grains	1 gram

Dissolve Elon in water before adding sodium sulphite; otherwise re-precipitation may occur.

This is a concentrated solution which will keep for months in filled, tightly corked bottles. For a working solution, dilute with two parts water for hard or contrasty papers or with four parts for normal and soft papers. Temperature of developer should be 65 deg. F.

Constrasty papers should develop quickly, twenty to forty seconds, while soft and normal papers will develop more slowly, forty to sixty seconds. The printing exposure should be so adjusted that development will be complete in the times specified. Too short exposure will require long development, giving cold, bluish tones; too long exposure will cause prints to flash up and darken before they can be removed from developer, giving muddy olive tones. If altering the exposure time does not remedy this, the addition of a few grains of caustic potash or soda to the developer will remove olive tones, and a few drops of 10 per cent solution of potassium bromide will correct blue tones.

When prints are fixed in the fixing bath given above, ten minutes are sufficient provided they are kept in motion. After fixing, wash in running water thirty minutes, or until permanganate test shows absence of hypo. Dry prints on a ferrotype plate or "squegee board" by placing them with surface down, covering with blotters and pressing into firm contact with a print roller. However, if the wash water is dirty or contains sediment, swab each print clean with a tuft of wet cotton before placing on ferrotype plate. When dry the prints may easily be stripped off, and will have a brilliant glossy surface which is very pleasing and which will show the finest details of the negative. Ferrotype plates should be kept clean and free from scratches. They may be washed with soap and water if necessary. Any tendency of prints to stick to the ferrotype plate may be overcome by rubbing its surface with a drop or two of three-in-one oil or paraffin dissolved in benzine, and polishing with a tuft of clean dry cotton or a soft cloth.

Trimming of Prints. — This is most easily done with a knife edge print trimmer to a size 3½ inches square or any other convenient size. Some prefer a circular shape, and this can be done by cutting the dry print with a revolving print trimmer and a metal mask. Care must be used with this method to avoid rough edges on the print. Circular prints may also be made on square sheets during printing, by placing a mask made of red or black paper between the negative and the light. If the printing mask is used it should not be placed between the negative and the paper. In the latter position, fine detail may be destroyed.

General Precautions. — Have a separate room set aside to be used for the dark room and for no other purpose. It should be provided with a wide bench along one wall with sink and running water at one end. A "safe light" over the sink and another at the other end of bench will be convenient, the latter for loading plate holders. Dust off plates with a soft camel's hair brush before loading, to prevent pinholes in the negative. Keep things in order, with a place for everything and everything in its place. Store negatives in paper envelopes with number, description, and other data on each one, and with a catalogue so that a given negative can be found quickly when wanted. Cleanliness is essential. Do not allow dried developer to collect around necks of bottles. Have a special tray or hard rubber fixing box for the fixing bath and use it for no other purpose. Never use a hypo tray for developing. Rinse fingers and hands after handling prints in fixing bath before again using the developer. Hypo is an excellent thing in a fixing bath, but a very bad one in the developer. If developers or fixing bath get spilled, wipe them up and do not allow dried crystals to blow around the dark room. In warm weather put developing tray into a larger one containing ice water and thus keep solutions at their proper temperature.

If possible printing should be done in a separate dark room where an orange or dark yellow light will suffice. An electric fan is a great convenience for hastening the drying of negatives and prints.

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PREPARATION OF IRON AND STEEL SPECIMENS FOR MICROSCOPIC EXAMINATION [1]

By Francis F. Lucas

Sometimes circumstances do not permit one to control the dimensions of the specimens selected for examination, but usually this may be done. To secure best results the writer believes a specimen should be in the form of a cylindrical column the height of which is about one-third the diameter. If the specimen is square or rectangular the height should be similarly proportioned with reference to the width and breadth. The reason for this is that it is difficult, and in some cases almost impossible, to polish a specimen flat if the height exceeds greatly the ratio expressed. Relative proportions of specimens are shown in Figures 464 and 465. Round speci-

[1] In view of the excellence of the high power photomicrographic work of Mr. Francis F. Lucas and of the care and skill required in preparing specimens for such work the readers, it is believed, will be grateful to Mr. Lucas for his kindness in describing his methods.

mens are preferred to square ones because corners are eliminated. When possible to do so it is well to bevel the edges of the specimen, as shown in Figure 466.

If wires are to be examined a blank of suitable proportions is selected and holes drilled through it into which the specimens are subsequently forced. To hold the specimens securely, holes are drilled laterally into the blank and tapped for set

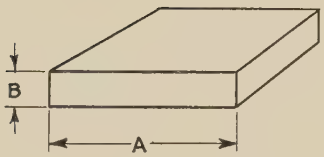

Fig. 464.

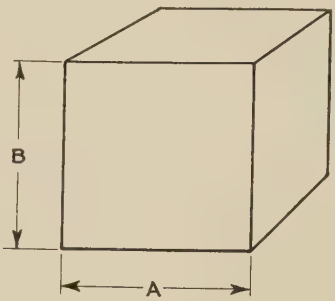

Fig. 465.

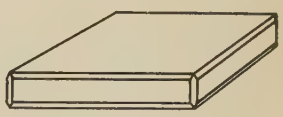

Fig. 466.

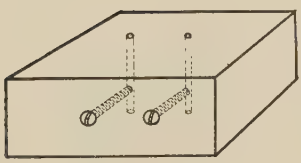

Fig. 467.

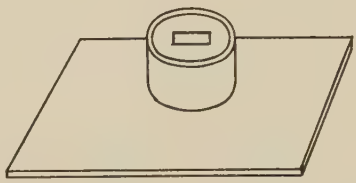

Fig. 468.

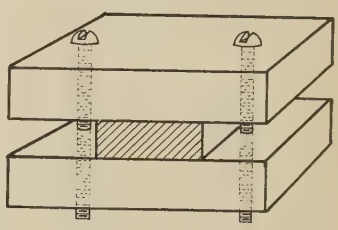

Fig. 469.

screws. These screws are forced tightly against the specimens and then the projecting portions are cut off so as to make the blank more convenient to manipulate in the fingers. The arrangement is illustrated in Figure 467.

Thin sheets or flat specimens are clamped between two blocks of metal of a hardness about that of the specimen itself. This method is illustrated in Figure 469.

Irregularly shaped specimens may be mounted in a fiber tube in the manner shown in Figure 468. Dry Canada balsam is heated quite hot in a covered beaker and when free from bubbles is poured into the mold provided by the tubing. The balsam solidifies, encasing the specimen in a hard, transparent, and glass-like resin. For some classes of work this method will be found quite convenient. Low melting-point alloys usually are recommended for this purpose, but the writer finds them objectionable because of their inability to "wet" thoroughly the specimen, thus leaving crevices around the specimen into which grit may lodge.

The unmounted or the mounted specimen (as the case may be) is provided with a flat surface either by filing, grinding, or lapping, as may be required. The importance of this step cannot be overestimated. If the specimen is hardened steel the work should be executed with great care, because the surface of the specimen may be tempered even though no elevation of temperature is apparent to the fingers. It is best to grind all hardened specimens under water, and even then to proceed with care. For lapping operations the writer uses a No. 29 medium P. Ke India stone and lubricating oil. A circular motion is imparted to the specimen by the fin-

gers and it is gradually revolved in the fingers as the lapping operation is continued.

After flattening the surface of the specimen the work is continued on French emery papers. The writer uses No. 3, No. 2, No. 1, No. 0, No. 00, and No. 000 papers, but usually the No. 3 and No. 2 papers are not required. As the work progresses from one stage to another the specimen is cleaned and it is then turned 90 degrees with reference to the direction last followed. This is in accordance with the general practice and hardly needs description in detail. However, the paper work must not be neglected or hurried, otherwise the final result is sure to be faulty. It is best to spend all the time required and remove carefully and thoroughly the preceding coarser polishing scratches. The only way to be sure that the scratches left by the preceding paper have been removed is to develop a new set of finer scratches in a different direction. Sometimes mixtures of paraffin and kerosene applied to the papers improve cutting properties, but usually it is best to avoid the use of oils unless care is later taken to remove all traces. The presence of paraffin or kerosene may interfere with the etching characteristics of the specimen and the activity of the reagent.

From the No. 000 paper the polishing of the specimen is continued on a horizontal lap, covered with ordinary grade of broadcloth and charged with No. 65-F alundum. About a teaspoonful of abrasive is placed at the center of the lap and spread with the fingers. Water is used sparingly and the lap is run at a speed of about 300 R. P. M. The specimen is first moved in and out along a radius with the No. 000 paper scratches parallel to the radius. The object is to develop a new set of scratches by the alundum and to remove completely all evidences of the No. 000 paper scratches. When these have been removed the specimen is slowly rotated clockwise about the lap, which should be arranged to run counter-clockwise (left-handed persons probably would find a reverse in the order of rotation more convenient). Rotating the specimen prevents the metal from building up, and thus gives sharp, clean outlines to inclusions.

The alundum lap will leave the specimen semi-polished, but the scratches will be very fine — no coarse scratches, streaks, or other imperfections being visible. The specimen and the hands are washed thoroughly to remove every bit of grit, and the final polishing operation is executed on another horizontal lap machine covered with a very fine grade of broadcloth known as "kitten's ear." Separate polishing machines for the alundum and final polishing operations are used to avoid contamination of the final abrasive by coarser ones.

About a tablespoonful of fine magnesium oxide is placed at the center of the lap and enough distilled water added to form a thick paste, which is rubbed out to cover a circular area on the lap about 3 inches in diameter. The lap is run at a speed of about 100 R. P. M. and the specimen is manipulated under very light pressure counter-clockwise or opposite to the direction of rotation of the lap. A few drops of distilled water should be added occasionally to keep the abrasive in a pasty condition.

If the work has been properly carried out the specimen will take on a brilliant white polish and no scratches should be seen at any magnification with objectives of highest resolving power.

When the magnesium lap is not in use it is best to keep the surface moist and to cover the lap with a clean towel. Grit and dirt from the air may contaminate the abrasive, and if the magnesium oxide paste is not kept moist it will become hard

and develop gritty particles. When in this condition the lap is useless. It must be washed thoroughly and soaked in water acidulated with hydrochloric acid. Each night the lap should be washed free from abrasive and stored in a covered vessel containing distilled water. A little hydrochloric acid added to the water keeps the cloth free from carbonates.

After the final polishing operation the specimen is washed under a tap of running water and the polished surface gently wiped with a clean absorbent cotton swab or with lens paper. Care and skill are necessary, otherwise the surface may be scratched. The writer then dries the rough surfaces of the specimen with a linen towel and the polished surface with lens paper. Final drying is accomplished in a mild stream of warm air.

Whenever possible mounted specimens should be taken from their mounts and thoroughly cleaned before etching. Specimens mounted in balsam should be removed because the balsam is soluble in the usual reagents used in etching.

For alcoholic etching reagents the writer employs three 50 cc. beakers arranged in a row. The first contains the reagent, the second 95 per cent alcohol, and the third absolute alcohol. In some cases a fourth beaker is used to contain another absolute alcohol bath. The specimen is etched the exact time required and then rinsed in the several alcohol baths in the order named. From the last bath it is placed immediately in a stream of warm air and dried. The specimen is then ready for examination.

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